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DETERMINATION OF NATURAL EXCHANGE
CONSTANTS OF OXYGEN IN OCEANIC SULPHATES

By

Ralph Rillman Miller

United States Naval Postgraduate School



THESIS

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CONSTANTS OF OXYGEN IN OCEANIC SULPHATES

by

Ralph Rillman Miller, III

Thesis Advisor:

C. F. Rowell

March 1971

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Determination of Natural Exchange
Constants of Oxygen in Oceanic Sulphates

by

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Lieutenant Commander, United States Navy
B.A., University of Washington, 1961

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requirements for the degree of

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from the

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ABSTRACT

An investigation was made into the rate of equilibration of the stable isotopes of oxygen in the water-sulphate system in the ocean. Two cores from the Carmel Submarine Canyon off the California coast were analyzed. The absolute ratios of the oxygen in the interstitial water and dissolved sulphates were determined using a mass spectrometer. The various biological and physical processes which can alter the isotopic ratios were discussed and a simple mathematical model was proposed. The mathematical model retained terms which were considered significant in the anaerobic zone of a sediment. After simple manipulations, a computational model was derived and a time constant for the oxygen ratio of the water-sulphate system was determined as -0.0150 ± 0.0029 (standard deviations) year^{-1} . From this, the $t_{1/2}$ was determined to be 46.2 years.

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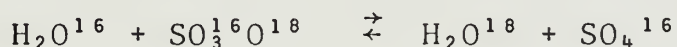
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I. INTRODUCTION

All elements in nature progress from states of lower entropy to states of higher entropy. Along the way to its final resting state, an element may be acted upon by many energy sources and be cycled through a nearly closed loop many times. At each step of these loops, the element is acted upon while being recombined into its next form in the loop. Oxygen exists naturally as three stable isotopes of mass weight 16, 17 and 18. Of these, O^{17} is found only in trace amounts so will not be considered further. As the stable isotopes of oxygen move from one chemical combination to the next, the ratio of one mass number to the other may vary accordingly. Some combinations, notably CO_2 , rapidly equilibrate with a new environment. Others, like NO_3^{2-} , PO_3^{3-} and SO_4^{2-} , take a relatively long time to exchange their oxygens and exhibit the oxygen isotopic ratio of their surroundings. The purpose of this paper is to investigate the rate at which sulphates, derived from a terrestrial source, come to equilibrium with the oxygen in ocean waters. If such a rate could be determined for the oceans, it would provide a way to date water masses without resorting to radioactive nuclides. The equation for this exchange is



The ratios of the O^{18} to O^{16} are defined as the oxygen ratio.

A. TECHNIQUE

Originally it was hoped that it would be possible to identify the water mass emanating from the Carmel River, California, follow it as it admixed with the ocean and then determine a rate of equilibration by knowing the age of the water mass. However, this method presented insurmountable difficulties in following a specific flood of the Carmel River any further than the first headland so it was decided that the sediments of the Carmel Submarine Canyon, which begins in Carmel Bay (Figure 1), offered a handy source of a time series of sufficiently long duration so that the time rate of equilibration of the water-sulphate system could be determined from the interstitial water and sulphate of a standard core. While there were many problems associated with the study of oxygen isotope ratios in the interstitial water-sulphate system of a core, it seemed a feasible choice. Carmel Canyon was chosen for study as it is relatively unexplored compared to the more familiar Monterey Submarine Canyon in Monterey Bay, just North of Carmel Bay, and the discharge of the Carmel River into it is relatively straightforward. The mouth of the Salinas River stagnates most of the year and thus greatly complicates the history of the sulphates it discharges into the head of the Monterey Canyon. Therefore two gravity cores were taken at the head of the Carmel Canyon (Figure 1). The interstitial water of these cores was analyzed for the oxygen ratios (the ratio of the O^{18} to the O^{16}) of the water and the dissolved sulphates.

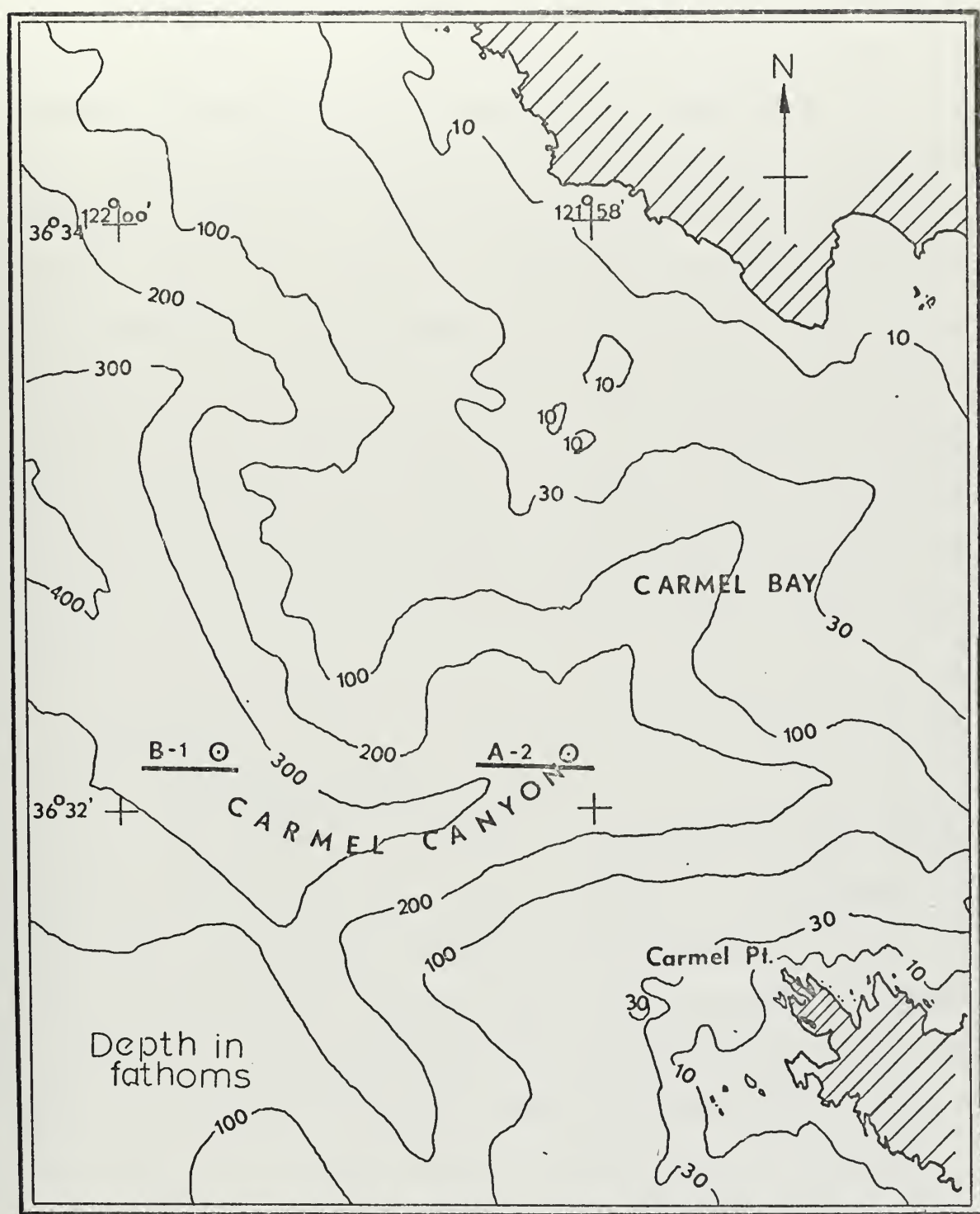


Figure 1. Locations of two cores taken in the Carmel Canyon.

These are reported herein as R_{H_2O} and R_{SO_4} respectively. In the literature absolute ratios of this type are not usually reported; rather, the ratio of the sample is compared to a standard of known isotopic composition. This is done because modern mass spectrometers used to determine isotopic abundances are of the double collector type which compare voltages from both collectors (unknown and standard samples) simultaneously. The voltages are thus directly convertible to relative ratios. This technique gives results accurate to four and five significant figures. The mass spectrometer used for the analyses in this investigation was of the single collector type and therefore isotopic abundance data is reported as the absolute ratios accurate to three significant figures.

B. HISTORICAL

1. Laboratory Studies

Few workers have addressed themselves to the problem of the rate of exchange of oxygen isotopes in sulphates. Teis (1956), Hoering and Kennedy (1956) and Lloyd (1967) tried to estimate and explain the rate of exchange of oxygen in sulphates. Teis estimated the rate of exchange to be such that complete equilibration occurred in about 350 years (5 half lives). He did not indicate the pH of his solutions but Lloyd presumed it to be low (about 3.2). Lloyd and Teis both let enriched sulphate solutions stand at elevated temperatures. Lloyd worked with higher pH's and let his samples

stand for up to 2 years. His data yielded an extrapolated time of equilibration of about 30,000 years at 4°C and a pH of 8.2. Hoering and Kennedy studied the exchange rate in strong sulphuric acid solutions (1f to 16f) where sulphuric acid is dissociated into the proton and bisulphate ion. They attempted to measure the rate of exchange as a function of acid concentration (activity). They demonstrated that the exchange rate is a function of pH and further that the dissociation of H_2SO_4 into $\text{H}_2\text{O} + \text{SO}_3$ is the rate-determining step of the equilibrium. This is a brief summary of the laboratory work which has been done. All of it has been done at temperatures much above the mean temperature of the ocean (4°C).

2. Field Work

Some field work by Rafter and Mizutani (1967) has been done to determine del values for oxygen in the dissolved sulphates and the water in Lake Vanda, a highly stratified saline lake in Antarctica. Their results are reproduced as Figure 2. Del values are reported relative to SMOW (Standard Mean Ocean Water) (Craig, 1957) where:

$$\delta\text{O}^{18} = \left(\frac{\text{O}^{18}/\text{O}^{16} \text{ sample}}{\text{O}^{18}/\text{O}^{16} \text{ standard}} - 1 \right) \times 10^3 \text{ ‰}$$

and the standard is sea water whose del value is zero. If some dates were available for the various layers of the Lake Vanda samples, a time constant could be calculated directly. It is suspected that the stratified portions of the lake

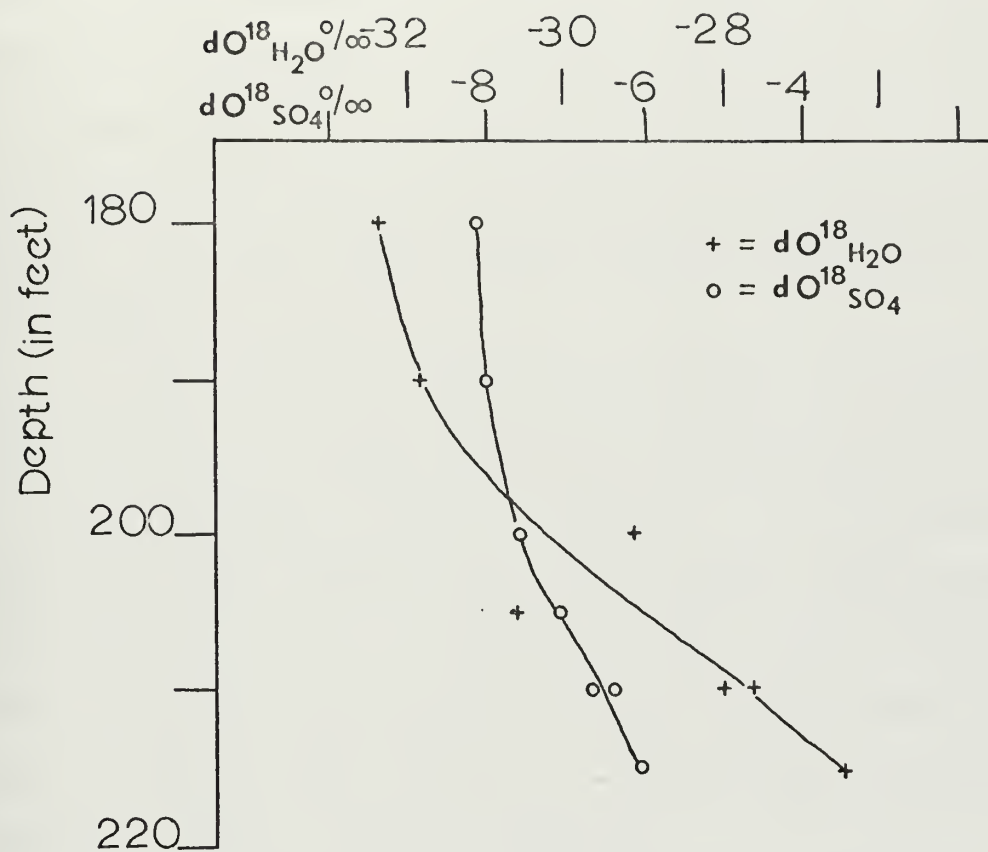


Figure 2. Oxygen isotope ratios of Lake Vanda water and sulphates versus depth. (After Rafter and Mizutani, 1967).

have remained non-convective for up to 50,000 years (Clark et al, 1969). The samples Rafter and Mizutani analyzed had been collected five years earlier by Wilson and Wellman (1962) and one might suspect that in that time span some equilibration could have occurred. However, Longinelli and Craig (1967), speaking of sea water samples from the Pacific, could find "no tendency for samples stored up to six years to change significantly in isotopic composition." It is presumed that the deeper layers represent progressively older waters. The water then becomes progressively heavier in O^{18} with depth.

Teis (1954) determined the isotope effect for certain crystals and their water of crystallization. He found, as one might expect, that the heavier O^{18} was preferentially taken up by the crystal lattices of gypsum, barium chloride and sodium sulphate. Bi-sodium sulphate showed little effect. Overall, one would then expect highly stable structures as the stratified layers of Lake Vanda to show a tendency to become lighter with age.

The sulphate oxygen in Lake Vanda also became progressively heavier with age with a linear slope approximately equal to 0.2 ‰/ft . Thus the water-sulphate system is being progressively depleted of O^{16} by some process other than that Teis investigated. Biological and physical processes as well as time exchange have probably operated on this water. One *Chlorella*-like alga was collected in these layers (Wilson and Wellman, 1962) and it is expected that a

commensal bacterial population exists. Eventually, if the sulphates and the ambient water are to equilibrate, they should reach the same del value or values whose ratio is constant. This would give a line of slope equal to one on a graph like Figure 3. Such a line has been drawn on Figure 3 as an extrapolation. It can be seen that the rate of change of the sulphate is greater than that of the water.

van Donk and Mathieu (1969) analyzed water samples from the American Basin of the Arctic Ocean. Below 300 m the waters of the basin are apparently non-convective and the salinity and δO^{18} (H_2O) are nearly constant with depth. The water approaches the isotopic composition of SMOW at great depth. Unfortunately no analyses were performed on the sulphates.

Rafter and Mizutani (1967) also investigated the oxygen values of a hot geothermal spring at Wairakei, New Zealand. This data, reproduced on Figure 4, shows that the water had a constant del value for all samples run of - 5.0 ‰ (relative to SMOW) and the sulphates had nearly the del value (relative to SMOW) of ± 2.0 ‰. Rafter and Mizutani assumed that this represented isotopic equilibrium between the sulphates and the water and calculated the theoretical temperature to be about 140°C. The measured temperature of the bore was around 270°C. They attributed the discrepancy to uncertainties in the theoretical isotopic equilibrium constants.

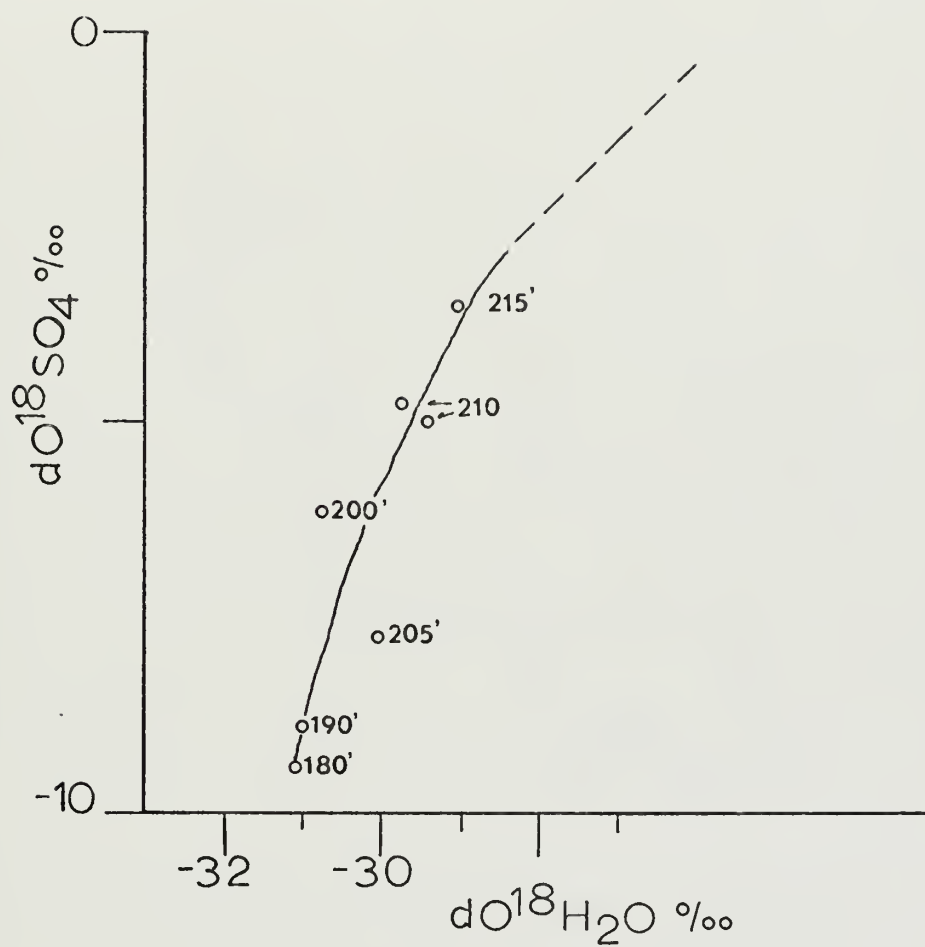


Figure 3. Correlation of δ^{18} values in sulphates and the associated water of Lake Vanda, Antarctica.
(After Rafter and Mizutani, 1967).

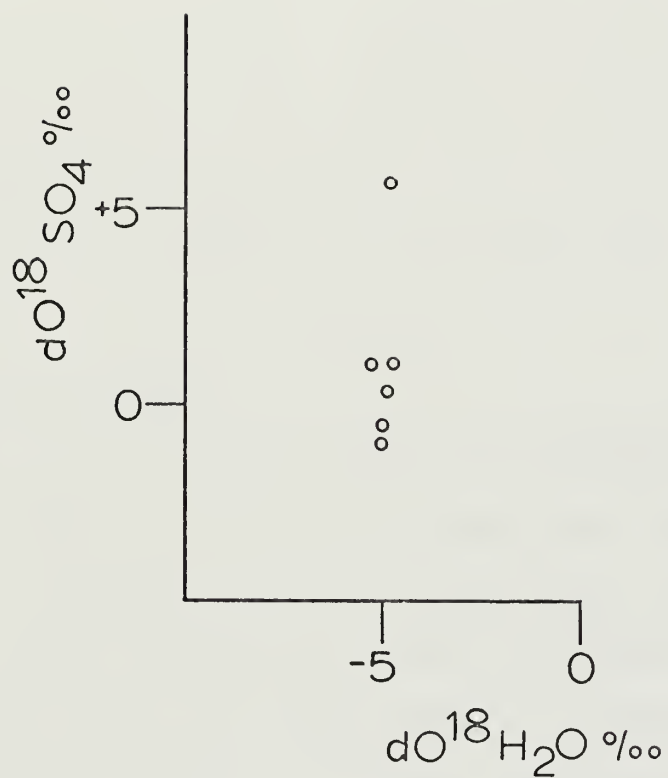


Figure 4. Correlation of δO^{18} values in sulphates and the associated water of a hot geothermal spring in Wairakei, New Zealand. (After Rafter and Mizutani, 1967).

II. EXPERIMENTAL PROCEDURE

A. SAMPLING PROCEDURE

Two gravity cores, 2.5 inch diameter and about 50 inches long, were taken from a fairly level area of the upper head of the Carmel Canyon (Figure 1). The cores were not extruded but were kept in their plastic liners until analyzed. The cores were frozen to prevent continuing bacterial activity and interstitial water migration. Prior to being frozen, the residual water atop the core in the barrel was sampled and was also frozen. The two cores were labeled A-2 and B-1.

B. EXPERIMENTAL METHOD

One core (A-2) was sawn lengthwise and each half was analyzed independently as cores A-2 and A-2b. Both cores (A-2 and B-1) had approximately 2 inch lengths cut out of them every 10 inches giving six samples per core plus the water taken from the top of each which was labeled top-of-core. The frozen sediment was thawed and diluted with approximately 250 cc of distilled water and then filtered and centrifuged to separate out the solids from the effluent. Approximately 10 ml of 0.1N NaOH and 10 ml of 0.1M AlCl_3 was added to the effluent to bring down the suspended clays in the water and the flocculant and adsorbed clays were centrifuged off. Approximately 20 ml of 0.1N HCl and 10 ml of 0.1M BaCl_2 were then added to the effluent and the precipitate (BaSO_4) was digested for a half hour. The use of a

centrifuge to wash the precipitate made digestion less necessary than if filtration had been used alone. The precipitate was then washed three times with distilled water and dried at 90°C overnight.

The BaSO₄ yield from this procedure varied from apparent volumes of 5 ml in the surface layers of the sediments to about 0.2 ml at the lowest depths (50 inches) in the sediment. After drying, the precipitate was ready to be reduced. The reduction was carried out as described by Clayton and Epstein (1967). A Lepel RF furnace was used to drive the reaction. Figures 5a and 5b lay out the experimental apparatus. The precipitate was mixed with 10 to 20 times the stoichiometric amount of spectrographic-quality carbon. Lamp-black was tried but residual organic compounds masked the desired results. The crucible and pedestals were turned from a rod of spectrographic-quality graphite. The crucible was fitted with a tightly fitting cover of graphite to ensure an even internal heat flux. A Leeds and Northrup hot wire optical pyrometer was used to calibrate the settings on the RF furnace necessary to give temperatures of 700°C and 1150°C.

The mixed precipitate and carbon was put in the crucible and the whole system was outgassed to about 4×10^{-4} mmHg by a mechanical pump backed by an oil diffusion pump. The RF furnace was turned on to 700 °C to outgas all volatile products and gasses which the chamber and sample may have picked up in handling. After the pressure dropped below 4×10^{-4} mmHg

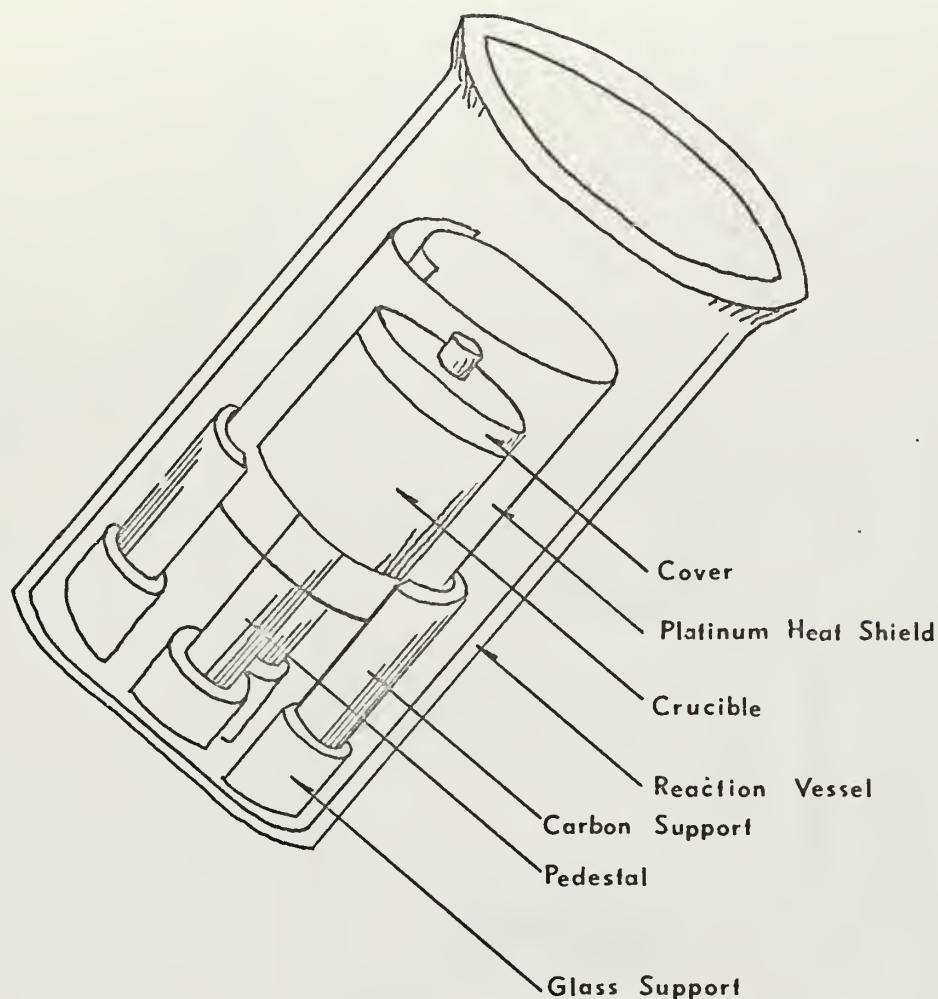


Figure 5a. Diagrammatic sketch of barium sulphate reduction chamber. The platinum shield is necessary to prevent the glass reaction vessel from melting. The platinum shield must form a complete loop but must not be closed so it does not itself become heated by the RF furnace.

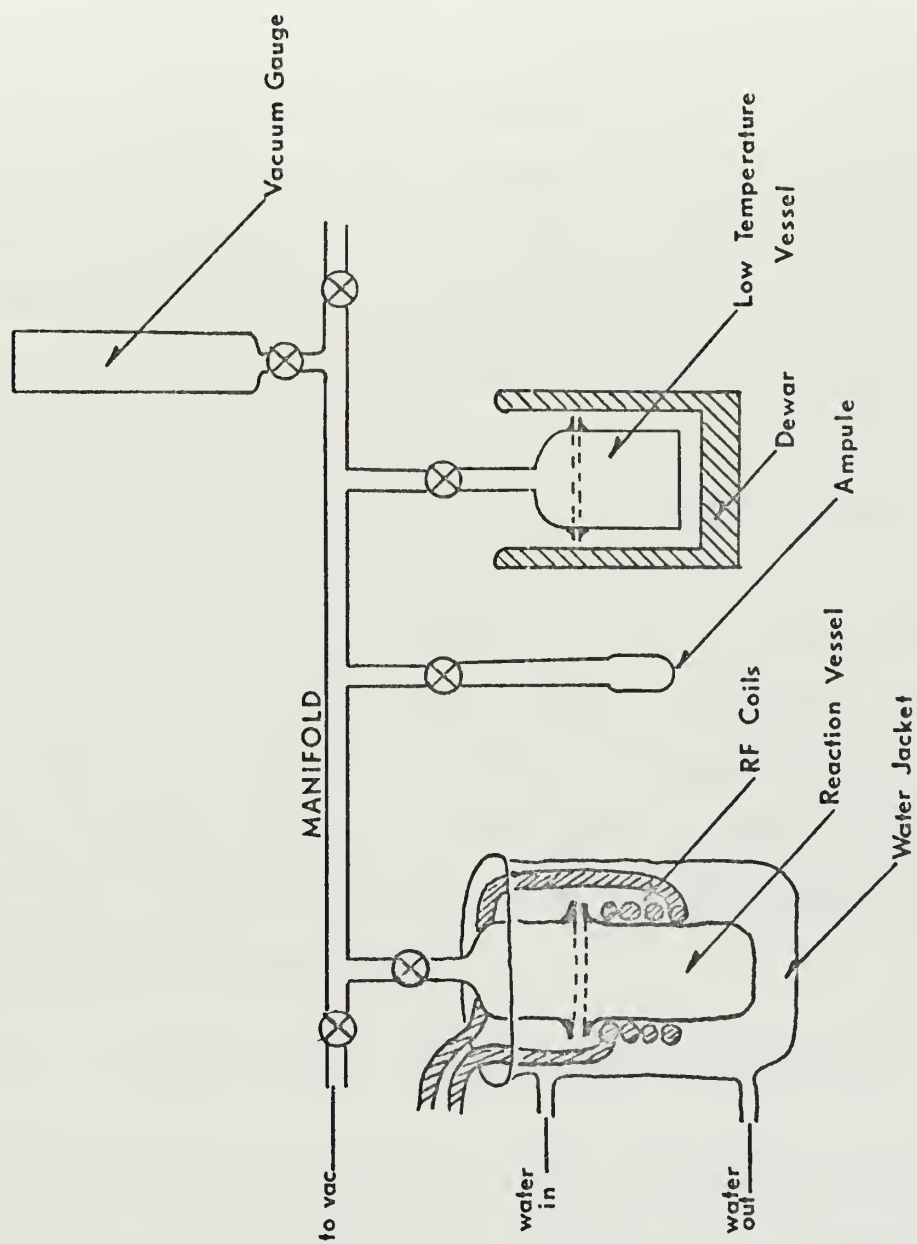


Figure 5b. Diagrammatic sketch of barium sulphate reduction chamber, low temperature vessel, and vacuum manifold.

(about 45 min.), the pumps were separated from the system and the heat increased to 1150°C. The reaction was allowed to proceed for 45 min. The carbon dioxide and carbon monoxide given off was collected in an ampule which was sealed with a torch at the end of the reaction period. The final pressures recorded were about 5 mmHg. The top-of-core water was handled in the same fashion since it generally had a large amount of suspended sediment.

The gas collected was analyzed on the Naval Postgraduate School mass spectrometer CEC type 21-103. This spectrometer is a single collector type and gives the absolute mass abundance ratios accurate to three significant figures. Since it was not possible to run samples against a known standard, all data is reported as the ratio of the mass peaks at 44 plus 45 versus 46. The mass ratios so derived are not the absolute ratios of oxygen since the carbon atoms were included in the ratios calculated. However the oxygen in each ratio can be easily determined.

$$R_{\text{SO}_4} \text{ (true)} = \frac{34/36}{32/34} \cdot R_{\text{SO}_4} \text{ (measured)}$$

Each ampule (depth) was used for three determinations of the ratio. These are listed as, for instance, 0 - 2 inches a, b and c in Table 3. Three determinations were needed to average out transient noise spikes in the zero line of the mass spectrogram.

Thus,

$$R_{SO_4} \text{ (measured)} = \frac{P_{46}}{P_{44} + P_{45}}$$

where P_a is the value of the mass peak at mass number a . The mass peaks at 44 and 45 constitute the sum of the O^{16} , O^{17} , C^{13} and C^{12} components and the 46 peak represents $C^{12}O^{16}O^{18}$. Craig (1957) indicated that, in del values, the correction for the mass ratio (C^{13}/C^{12}) of the carbon used is around one percent. Since this is on the order of accuracy of the mass spectrometric data used, it was therefore not included herein.

In order to determine the mass ratios of oxygen in the interstitial waters, the frozen sediment was first carefully scraped to remove the exterior layers. Then the frozen sediment was put in a vacuum vessel and kept frozen by liquid nitrogen while the vessel was outgassed. When the pressure was less than 3×10^{-4} mmHg, the system was closed off and allowed to come to room temperature overnight. The water vapor and other gasses given off were collected and analyzed on the mass spectrometer like the sulphate samples. The water ratios are reported as a fraction of the ratio between the mass 18 peak plus the mass 19 peak versus the mass 20 peak. Analogous to the sulphate ratios, a correction must be accounted for because of the hydrogen in the samples. This can be shown to be:

$$R_{H_2O} \text{ (true)} = \frac{18/20}{16/18} \cdot R_{H_2O} \text{ (measured)}$$

where again,

$$R_{H_2O} \text{ (measured)} = \frac{P_{20}}{P_{18}}$$

The mass peak at 19 was more than 100 times smaller than the mass peak at 18 and, therefore, not included.

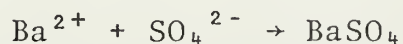
C. WATER CORRECTION

For a single-stage distillation process at 15 to 20°C the water vapor has a δO^{18} of -8‰ and δD^2 of -4‰. This assumes that the evaporation and condensation of the water takes place under conditions of thermodynamic equilibrium, and the D^2 and O^{18} content in the liquid and gaseous phases is controlled by the vapor pressures as in Rayleigh distillation (Rankama, 1963). Therefore the absolute ratio of water vapor should shift -1.2×10^{-5} per ‰. This is the correction factor for water at 20°C; however, since the data in this investigation was accurate only to $\pm 10 \times 10^{-5}$, it was ignored.

D. CHEMISTRY OF SULPHATE ANALYSIS

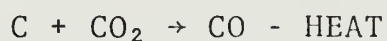
As the clays and silts are laid down on the Carmel Canyon floor, water adsorbed on such particles and carried down with them is collected in the sediments as interstitial water. Some of this water is carried down the canyon by the predominantly down-canyon transport from the main fresh water source in the area - the Carmel River. Thus the sulphates in the interstitial waters of the canyon's sediments are derived from the surface waters of the California coast and

the Carmel River. The derived water samples were slightly acidified to insure that the one barium salt to come down was BaSO₄ according to the equation:



Other salts, including borates, are too soluble to be brought out of solution. Thus, oxygen in the sulphates was fixed as the precipitated barium sulphate.

The washed precipitates were mixed with at least ten times the amount of carbon needed for complete reaction. The reduction was carried out in a carbon crucible. The following equations describe the products of this reduction:



Longinelli and Craig (1967) and Rafter (1957) have discussed the temperature dependence of these reactions. In general lower temperatures (1000°C) of reaction produce more carbon monoxide whereas at higher temperatures (1150°C) less carbon monoxide is produced.

A series of analyses were run on pure carbon dioxide and on air to determine the breakdown of the main component and possible contaminants to the analysis. Each sample was tested through the range of operating pressures of the ion chamber in the mass spectrometer. The results of these tests are depicted in Table 1. The National Bureau of Standards published spectral data on Argon, CO₂, CO and O₂ (American

Petroleum Institute Research Project 44, 1960) are presented in Table 2.

Table 1

Mass Spectral Data for Air (at different pressures)

Mass Number	14	16	18	28	29	32	40	44
Intensity	106.5	31.4	-	1248	9.0	259.0	28.3	-
Pressure	19.89 microns							
Intensity	195.3	57.6	2.9	2394	17.9	490	56.5	3.5
Pressure	17.95 microns							
Intensity	309	90.6	5.6	3980	29.6	825	98.4	-
Pressure	17.20 microns							
Intensity	361	35.3	5.8	4790	35.6	987	112.2	7.9
Pressure	20.83 microns							
Intensity	394	116.7	6.3	5160	38.3	1065	120.3	8.4
Pressure	19.89 microns							
Intensity	387	115.8	6.8	5000	37.6	1041	117.3	8.5
Pressure	18.97 microns							

Table 2

Published Mass Spectral Data

ARGON

Mass Number	20	36	40
Relative Intensity	13.0	0.32	100

CARBON DIOXIDE #157

Mass Number	12	16	28	29	44
Relative Intensity	6.67	9.40	8.17	0.10	100

1582

Mass Number	16	22	28	29	44	45	46
Relative Intensity	5.57	1.36	6.70	0.14	100	1.12	0.39

1596

Mass Number	12	16	22	28	44	45	46
Relative Intensity	2.46	6.24	1.78	6.55	100	1.16	0.41

CARBON MONOXIDE

Mass Number	12	14	16	28	29	30
Relative Intensity	4.71	0.75	1.67	100	1.16	0.22

Mass Number	14	28	29
Relative Intensity	5.18	100	0.73

OXYGEN

Mass Number	16	32	33	34
Relative Intensity	5.13	100	0.08	0.41

III. RESULTS

A. CORE B-1

The sulphate ratios with depth and the overlying water had a range of R_{SO_4} of $43.1 \times 10^{-4} \pm 0.9$ (Table 3). Plotted against depth (Figure 6) they fell on a complex line. There was fractionation apparent between the overlying waters and the sediment water interface. The sulphates in the top layers of the sediment columns were rejecting the O^{18} and retaining O^{16} . There was an inclusion of the heavier O^{18} or an exclusion of the lighter O^{16} between the surface layers and the 10 inch depth. Then from 10 inches to 30 inches inclusive, the R_{SO_4} was constant at $43.5 \pm 0.2 \times 10^{-4}$. At 40 and 50 inches there was a slight lightening of the sulphates as the R_{SO_4} dropped to 42.7×10^{-4} . Therefore, in this region some mechanism(s) was (were) operating to include more of the light O^{16} or to reject more of the heavy O^{18} from the interstitial sulphate ions.

The results of the water analysis showed interesting variations with depth which tended to correspond to the sulphate analysis. The top-of-core water (Figure 7 and Table 4) representing overlying water, was lighter than that from the top sediment layers, thus water which came down as interstitial water in the sediments was preferentially heavier or was acted upon immediately to fractionate out the O^{16} . In the first 10 inches of the sediment, the water

Table 3

 R_{SO_4} Core B-1

DEPTH IN CORE (Inches)	$R_{(measured)}$	Average	$R_{(true)}$
Top of Core	a. 41.0 b. 40.6 c. 41.9	41.2	43.8
0 - 2	a. 41.6 b. 40.1 c. 37.5	39.7	42.2
10	a. 40.8 b. 40.8 c. 40.7	40.8	43.4
20	a. 41.2 b. 40.4 c. 41.0	40.9	43.5
30	a. 40.9 b. 40.7 c. 40.9	40.9	43.5
40	a. 40.6 b. 40.5 c. 38.8	40.5	43.0 --Disregarded due to noise level
50	a. 41.6 b. 40.5 c. 39.9	40.2	--Disregarded 42.7 due to noise level

(All values of R_x are presented $\times 10^4$)

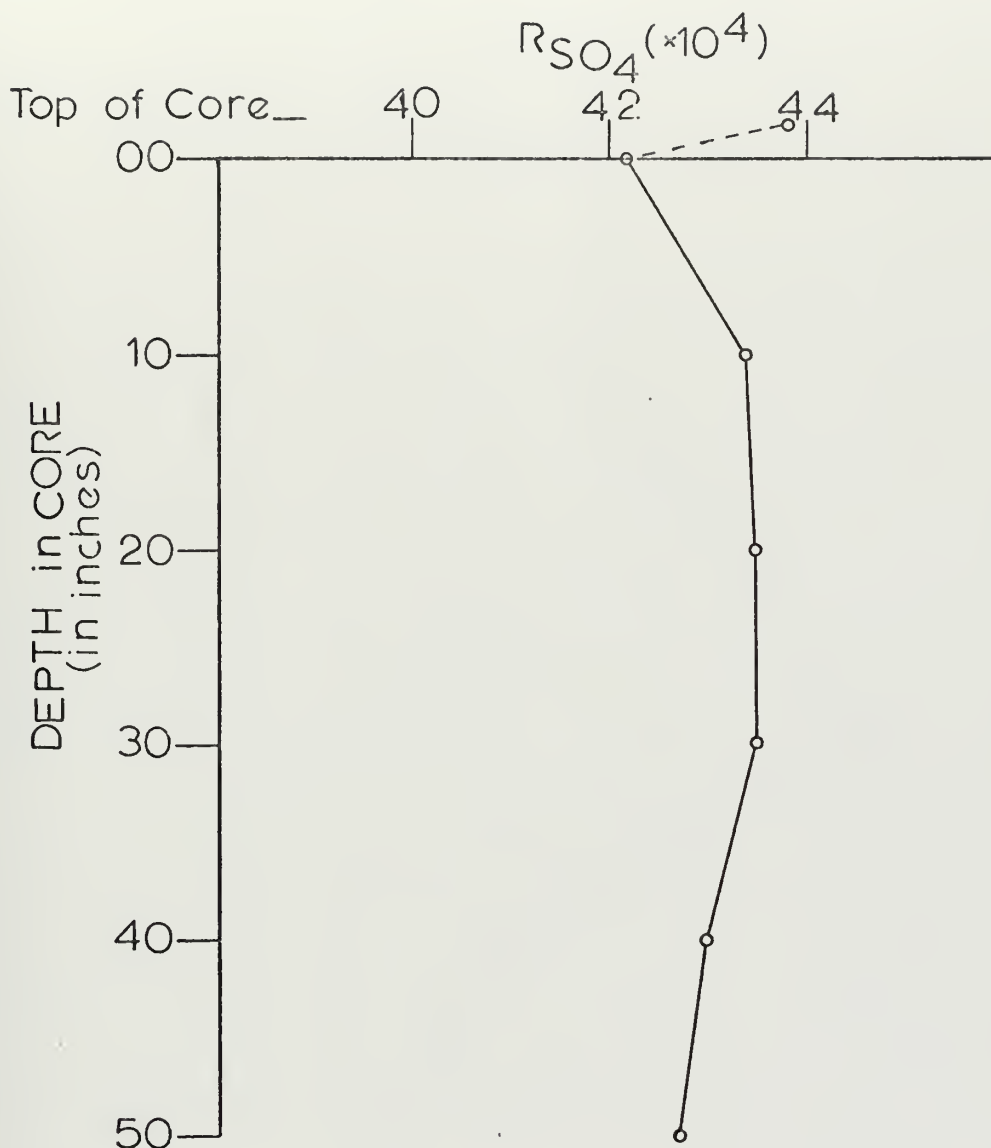


Figure 6. Absolute oxygen ratios in sulphates of core B-1 versus depth.

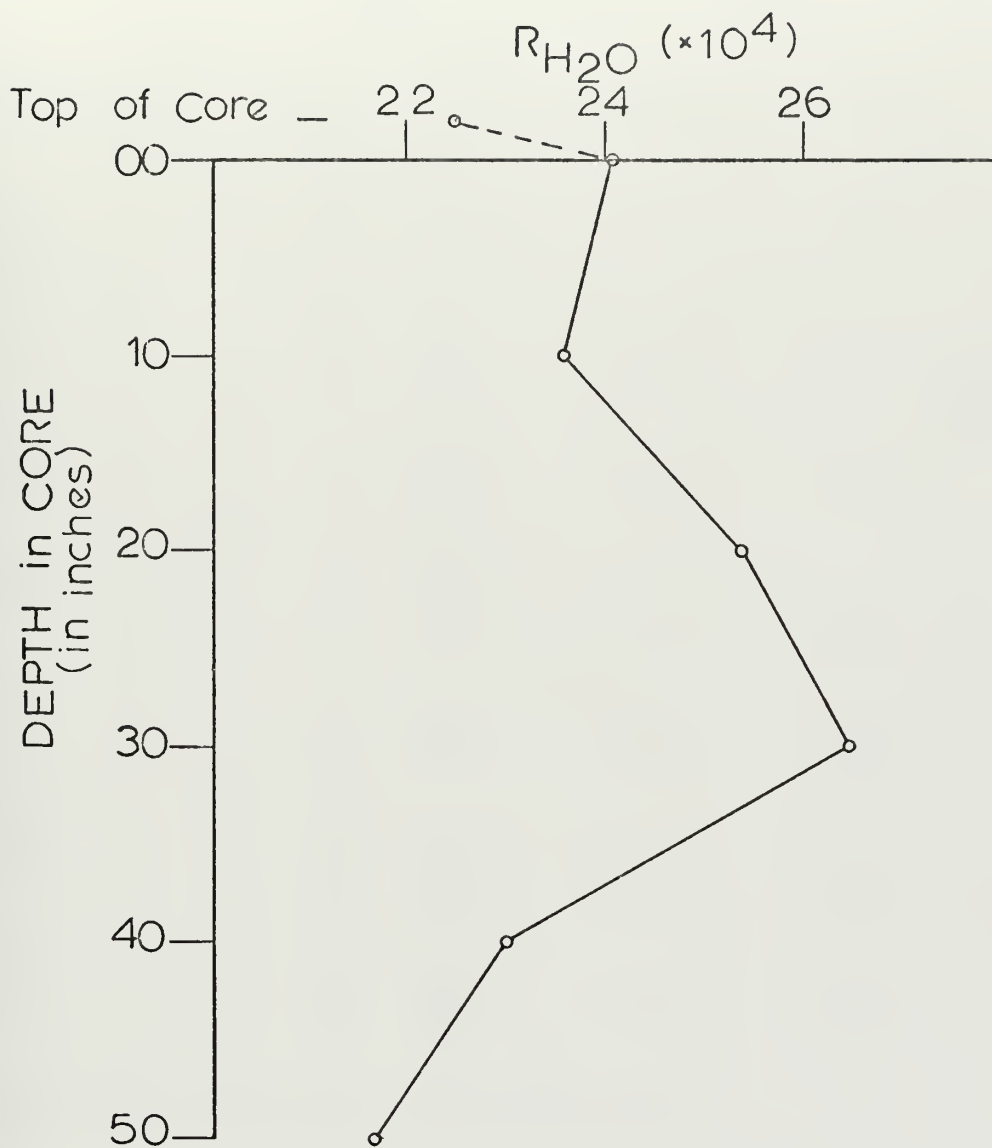


Figure 7. Absolute oxygen ratios in water of core B-1 versus depth.

Table 4

 R_{H_2O} Core B-1

Depth in Core (Inches)	$R_{(measured)}$	Average	$R_{(true)}$
Top of Core	a. 22.4 b. 21.6 c. 22.8	22.3	22.5
0 - 2	a. 23.5 b. 20.9 c. 24.1	23.8	24.1--Disregarded due to noise level
10	a. 22.8 b. 23.1 c. 24.6	23.3	23.6
20	a. 24.8 b. 25.5 c. ----	25.1	25.4
30	a. 26.2 b. 26.1 c. ----	26.2	26.5
40	a. 22.6 b. 22.3 c. 23.6	22.7	23.0
50	a. 20.9 b. 21.0 c. 22.4	21.4	21.7

(All values of R_x are presented $\times 10^4$)

appeared to remain essentially constant or slightly lighter at $R_{H_2O} = 24.1 \times 10^{-4}$. Then in the next 20 inches of core from 10 to 30 inches, the R_{H_2O} ratio increased almost linearly to 26.5×10^{-4} . In this region some combination of factors was operating to remove the lighter O^{16} from the interstitial water or add the heavier O^{18} . Below 30 inches the water became progressively lighter with depth falling from a ratio of 26.5×10^{-4} at 30 inches to 21.7×10^{-4} at 50 inches. Therefore, in this region the heavier O^{18} was being taken from the water or the lighter O^{16} added to it. Figure 8 summarizes the relative change in O^{16} with depth for the water-sulphate system of core B-1.

B. CORE A-2

Core A-2 (Figures 9 and 10, and Tables 5 and 6) was the first to be analyzed and, due to inexperience in handling and the fact that the mass spectrometer had a higher noise level than when samples from B-1 and A-2b were run, had a wider scatter in data points than core B-1. This greatly complicated a discussion of results from this core. General outlines relative to core B-1 could be drawn, however.

The sulphate ratio determined from the overlying waters for the two cores was about the same and a value of 43.5×10^{-4} was adopted as representative of the sulphates of the overlying waters. The surface layers of the sediment had about this ratio within the spread of data values obtained. Between the surface layers and 10 inches the sulphate became

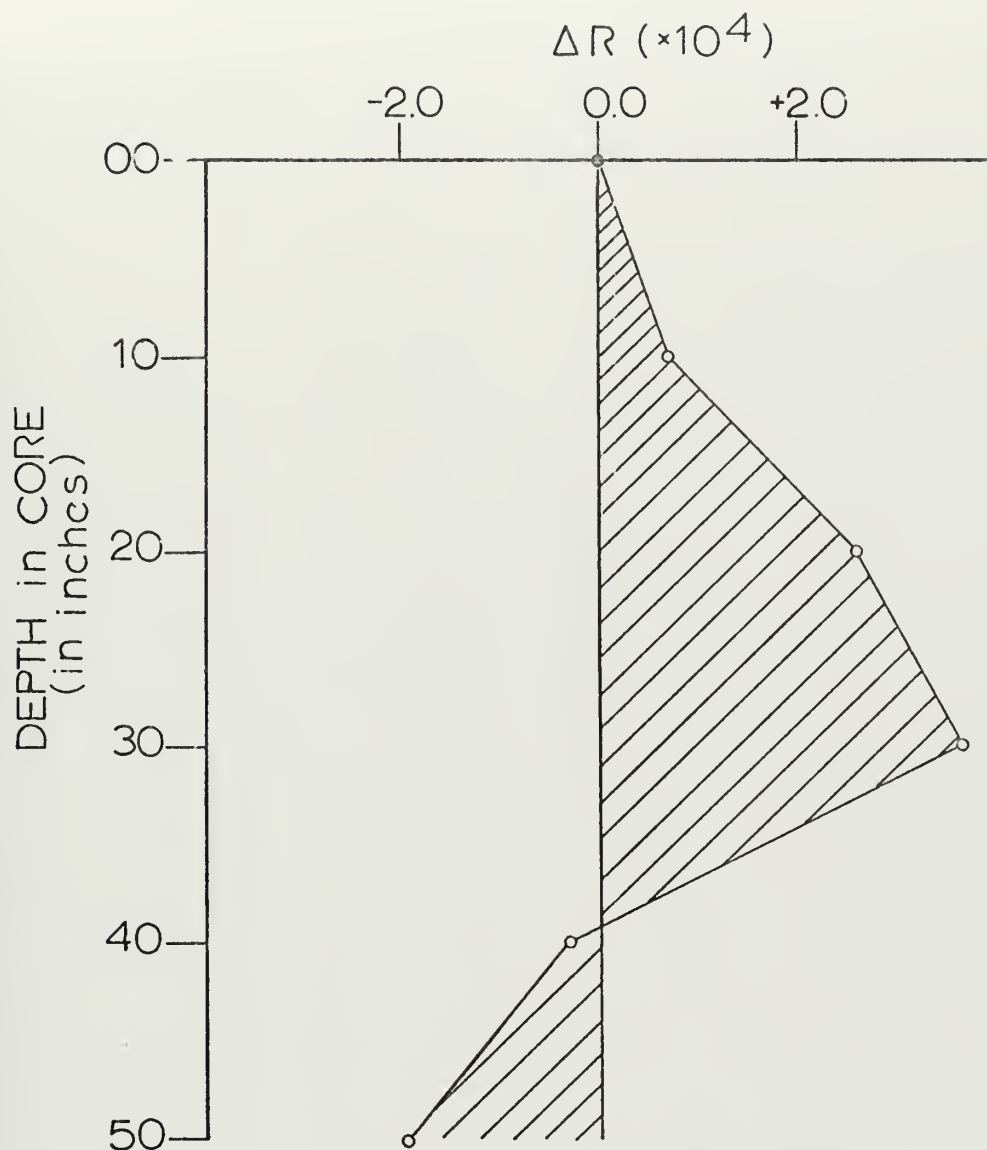


Figure 8. The loss or gain of oxygen versus depth for the water-sulphate system in core B-1. $\Delta R = [(R_{SO_4} \text{ (surface)} - R_{SO_4} \text{ (depth)}) + (R_{H_2O} \text{ (surface)} - R_{H_2O} \text{ (depth)})] \times 10^{-4}$

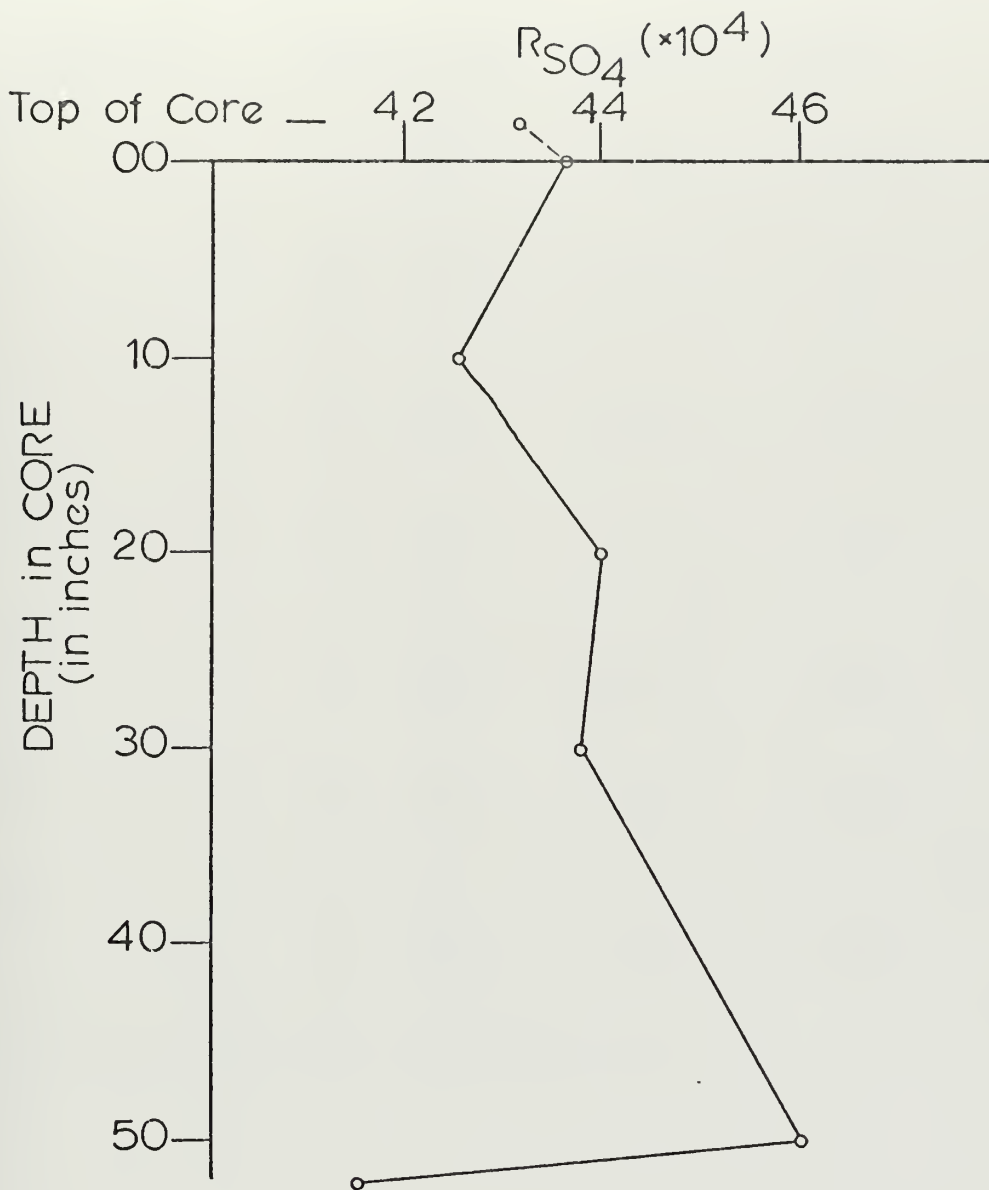


Figure 9. Absolute oxygen ratios in sulphate of core A-2 versus depth.

Table 5

 R_{SO_4} Core A-2

Depth in Core (Inches)	$R_{(measured)}$	Average	$R_{(true)}$
Top of Core	a. 40.9 b. 40.6 c. 40.6	40.7	43.2
00	a. 40.6 b. 41.8 c. 41.2	41.2	43.7
10	a. 41.5 b. 39.8 c. 39.0	40.1	42.6
20	a. 42.2 b. 41.0 c. 41.1	41.4	44.0
30	a. 41.7 b. 40.8 c. 41.2	41.2	43.8
50	a. 44.2 b. 42.5 c. 42.3	43.0	46.0
52	a. 40.7 b. 37.8 c. 38.8	38.8	41.5

(All values of R_x are presented $\times 10^4$)

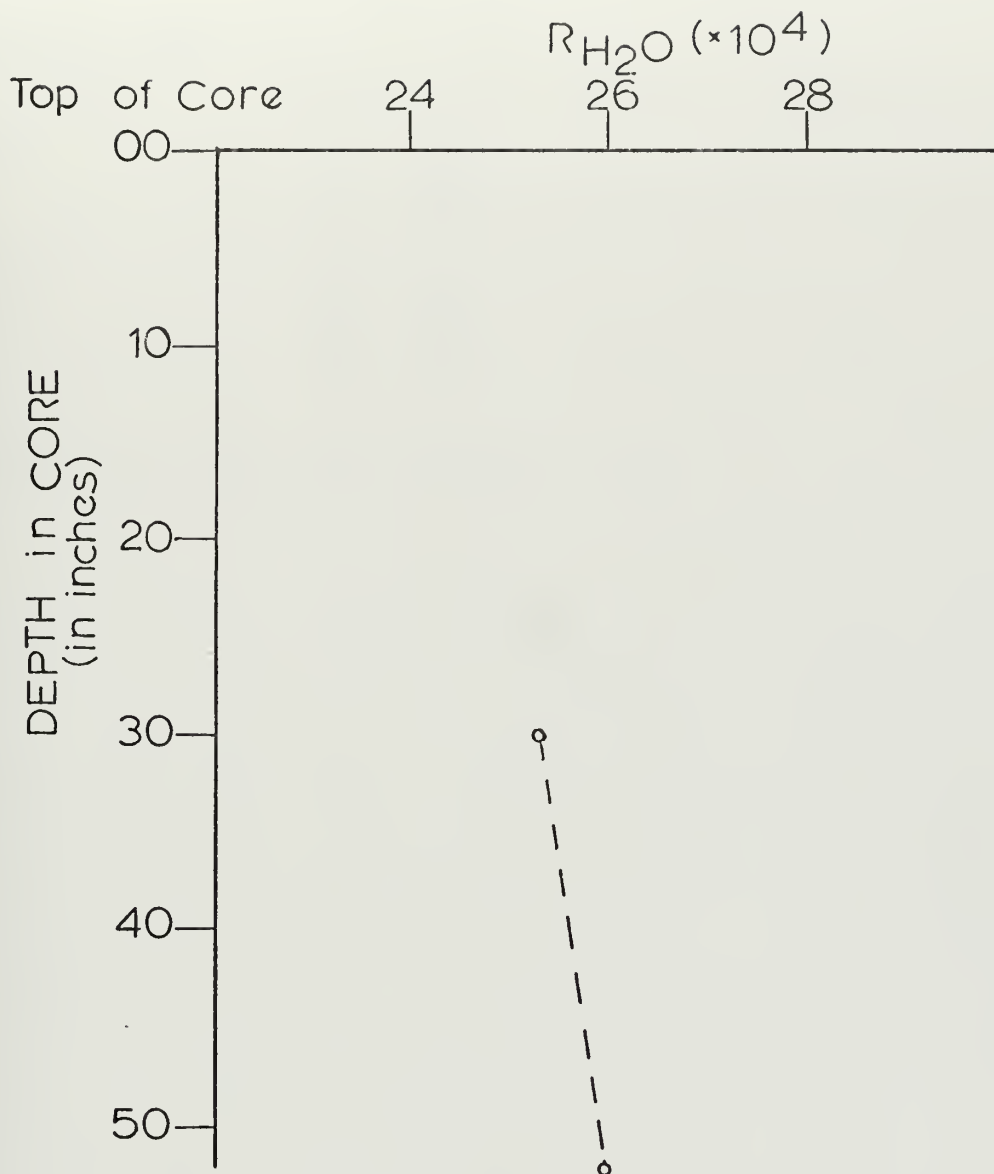


Figure 10. Absolute oxygen ratios in water of core A-2 versus depth.

Table 6

 R_{H_2O} Core A-2

Depth in Core (Inches)	$R_{\text{(measured)}}$	Average	$R_{\text{(true)}}$
30	a. 23.8	24.9	25.3
	b. 24.8		
	c. 26.3		
52	a. 24.1	25.5	25.9
	b. 26.0		
	c. 25.5		
	d. 26.6		

(All values of R_x are presented $\times 10^4$)

lighter. Then between 10 and 20 inches the ratio increased to about 43.7×10^{-4} and was constant to 30 inches. The bottom sampling depths of the core were not taken as representative of the core since it appeared that the bottom of the core had some extra water frozen in with it.

The interstitial water analyses from A-2 were inconclusive because of the lack of data points.

C. CORE A-2b

Core A-2b was the last series of analyses run and the increased level of experience in sample handling was reflected in a tighter grouping of data points (Figures 11 through 13 and Tables 7 and 8). Core A-2 was taken about a mile and a half up the canyon from core B-1. This is reflected in the analysis of the core which showed a more complicated picture than did B-1. The relatively constant integrated value of total O^{16} was interpreted to mean that the processes which act to remove or add O^{16} were acting approximately in equilibrium and therefore authigenic mineral formation was probably not occurring. Over the whole core, the water-sulphate system appeared to have lost a little O^{16} relative to the surface (Figure 13). Coming from a location nearer the coast, a deeper aerobic layer was expected. Below 40 inches, the system was probably beginning to behave more like B-1, with the water ratios moving to the left and the sulphate ratios beginning to respond to reach this new equilibrium.

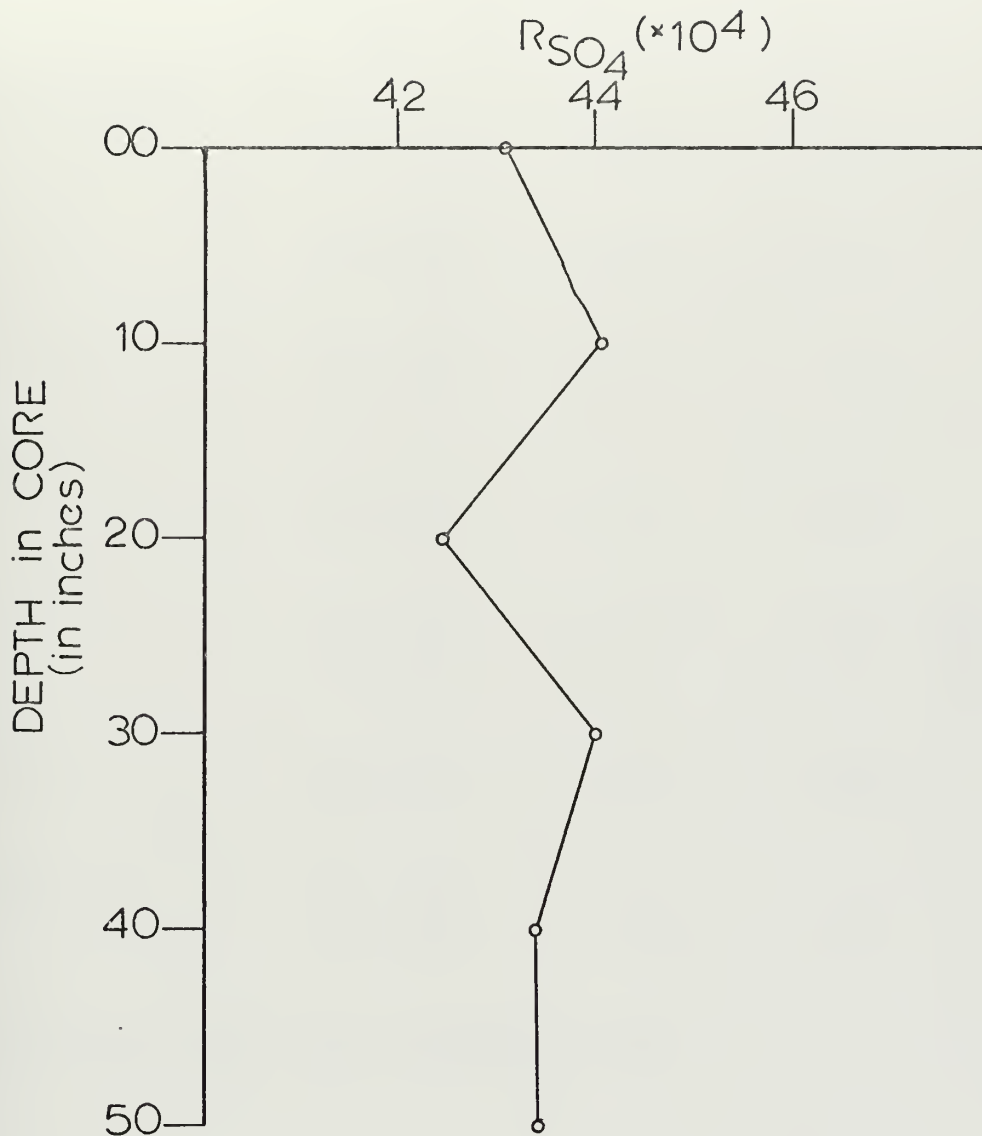


Figure 11. Absolute oxygen ratios in sulphate of core A-2b versus depth.

Table 7

 R_{SO_4} Core A-2b

Core in Depth (Inches)	$R_{(measured)}$	Average	$R_{(true)}$	
0 - 3	a. 41.1 b. 40.6 c. 40.3	40.6	43.1	
9 - 12	a. 42.0 b. 41.3 c. 41.1	41.5	44.1	
19 - 21	a. 41.0 b. 40.1 c. 39.8	40.0	42.5	
29 - 31	a. 42.1 b. 40.9 c. 41.3	41.4	44.0	This ampule may have had air contam- ination.
39 - 41	a. 40.6 b. 40.7 c. 41.2	40.8	43.4	
49 - 51	a. 40.9 b. 40.2 c. 41.3	40.8	43.4	

(All values of R_x are presented $\times 10^4$)

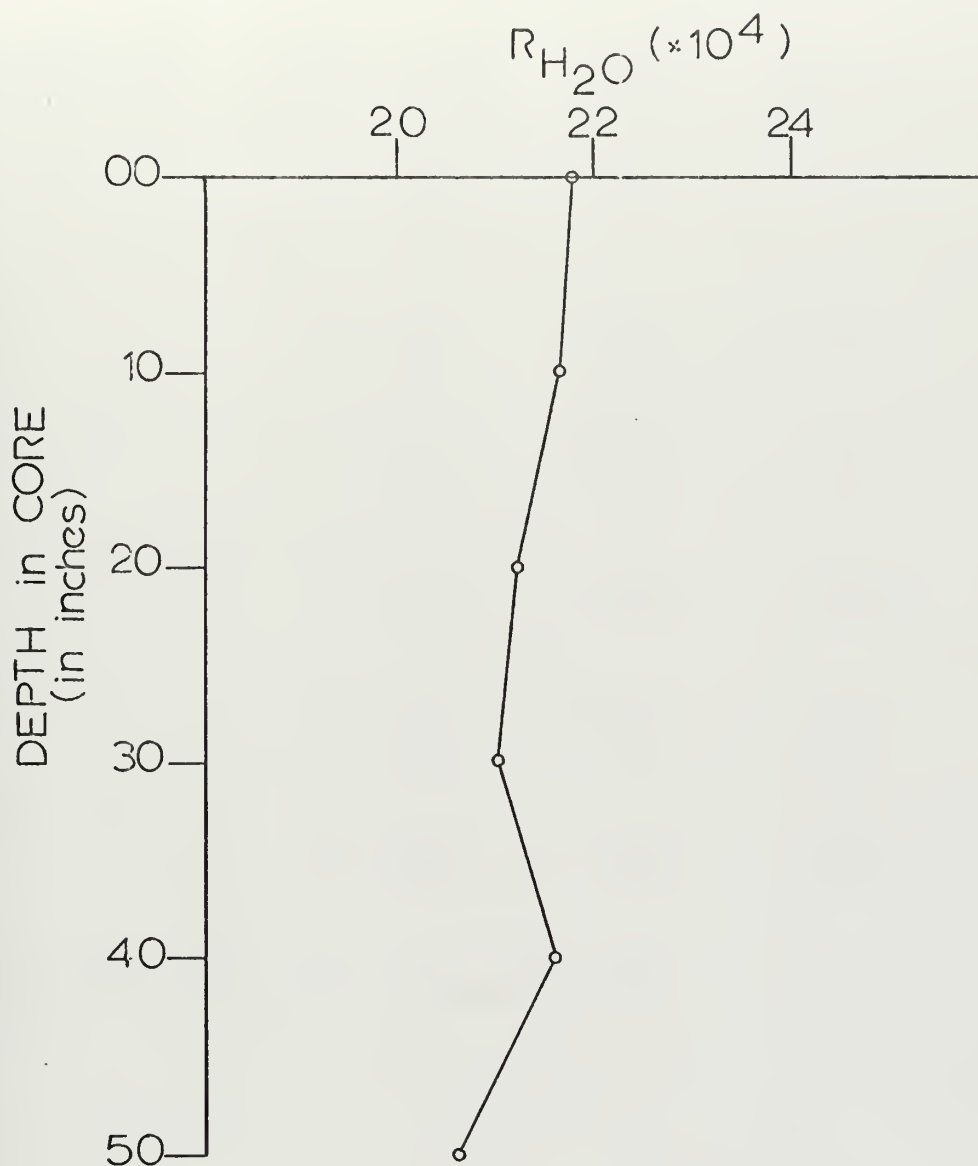


Figure 12. Absolute oxygen ratios in water of core A-2b versus depth.

Table 8

 R_{H_2O} Core A-2b

Depth in Core (Inches)	$R_{(measured)}$	Average	$R_{(true)}$
2 - 3	a. ----		
	b. 21.6	21.5	21.8
	c. 21.4		
10 - 11	a. ----		
	b. 21.5	21.4	21.7
	c. 21.4		
19 - 20	a. 20.7		
	b. 21.1	20.9	21.2
	c. 20.8		
31 - 32	a. 20.7		
	b. 21.3	20.7	21.0
	c. 20.2		
41 - 42	a. 21.6		
	b. 21.5	21.3	21.6
	c. 20.8		
48 - 49	a. 20.2		
	b. 20.5	20.3	20.6
	c. 20.1		

(All values of R_x are presented $\times 10^4$)



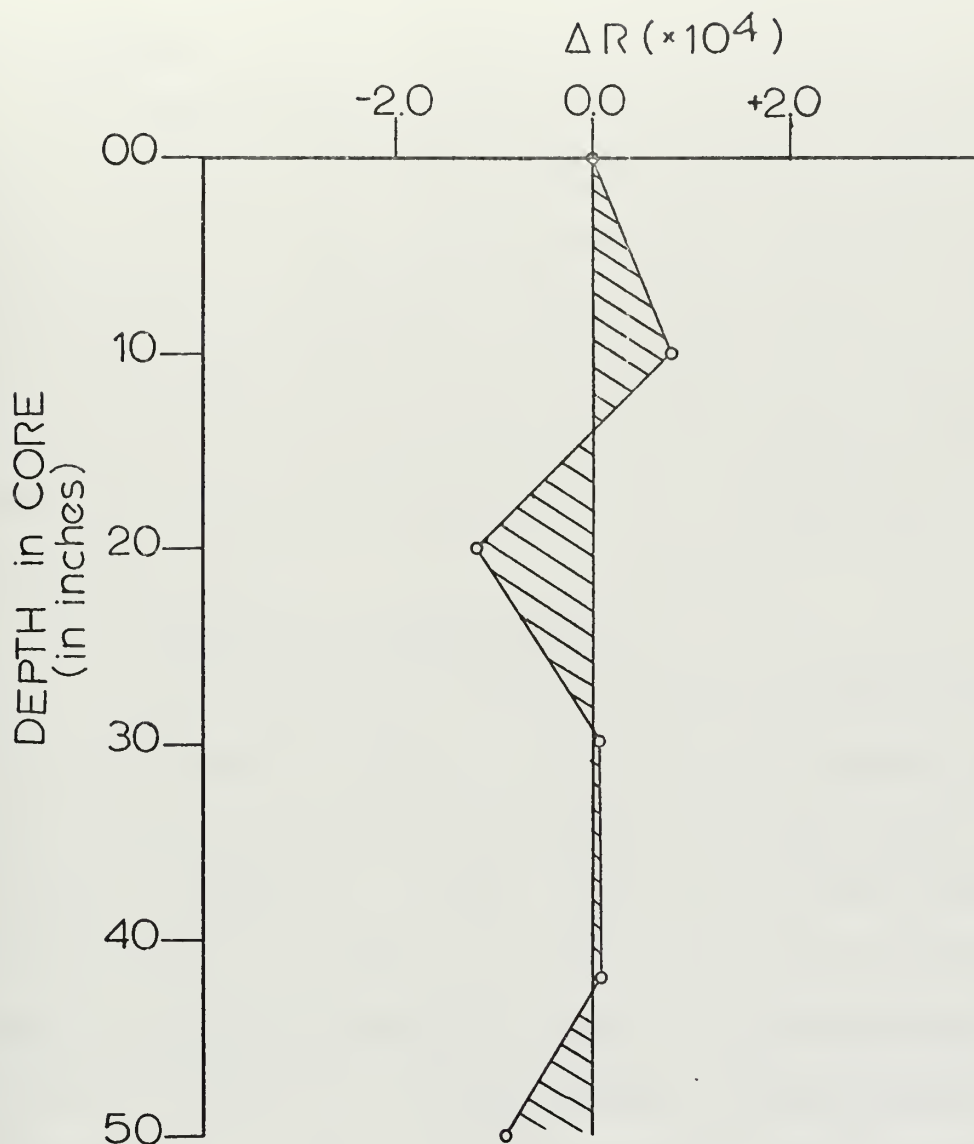


Figure 13. The loss or gain of oxygen versus depth for the water-sulphate system in core A-2b. $\Delta R = [(R_{SO_4} \text{ (surface)} - R_{SO_4} \text{ (depth)}) + (R_{H_2O} \text{ (surface)} - R_{H_2O} \text{ (depth)})] \times 10^4$

IV. DISCUSSION AND THEORY

A. GENERAL

The underlying principle that one uses in following a suite of isotopes through a chemical system is that the lighter isotopes react more rapidly than the heavier when bond-breaking predominates. Thus, a process which acts to place the oxygen (in this investigation) in a different energy state will tend to fractionate the parent population leaving O^{18} behind and removing O^{16} , or vice versa if bonds are being formed.

1. Biological Isotope Effect

Microorganisms (bacteria) exert a strong influence on the geochemical sulphur cycle and it is expected that they will likewise influence the geochemical oxygen cycle as it pertains to sulphates. There are bacteria which oxidize sulphur and its inorganic compounds both photosynthetically (Thiorhodaceae, Chlorobacteriaceae and Athiorhodaceae) and non-photosynthetically (Beggiatoaceae, Achromatiaceae and Thiobacillus). There are those bacteria which reduce sulphates to hydrogen sulphide (Desulfovibrio and Sporovibrio) and there are those which reduce organic sulphur compounds to H_2S (various pathogenic and saprophytic types like Proteus, Serratia and Clostridium) (Frobisher, 1957).

Of the bacteria which form sulphate from reduced sulphur, most require free oxygen to live. An example of

an aerobic Thiobacillus reaction would be



which is the overall reaction for Thiobacillus thioparus.

There is also an important group of sulphate producing bacteria which do not need oxygen but can utilize nitrates as an energy source. A common one found in soil is Thiobacillus denitrificans; its overall reaction is

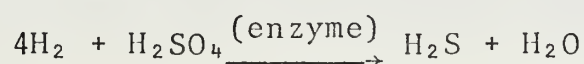


Frobisher points out that the thionate bacteria can occur where sulphur and its compounds occur as a result of chemical action or due to protein decomposition of the sulphate reducing bacteria Desulfovibrio. It is of some importance here to note that the thionate and nitrophilic bacteria use water in their reactions as well as thionate, oxygen, sulphur and nitrates, thereby establishing oxygen exchange with the ubiquitous solvent.

The sulphate reducing bacteria are divided into two genera. Sporovibrio, however, is thought to be only a spore-forming variant of Desulfovibrio. The fresh water specie D. desulfuricans is a strict anaerobe and heterotroph. Its overall reaction can be expressed as



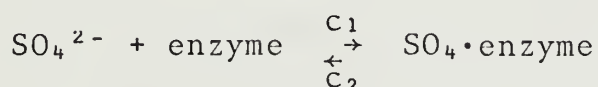
Notice that two end products are carbon dioxide and water. Some sulphate reducers are autotrophic and can directly reduce inorganic sulphates by means of the enzyme hydrogenase



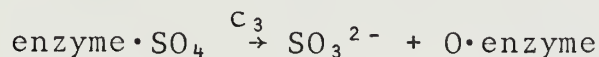
Again, water is an end product. The photosynthetic reactions will not be considered due to the location of the samples.

There have been a considerable number of laboratory studies done on the fractionation of sulphur in the biological reactions discussed above. Nakai and Jensen (1964) investigated the biological isotope fractionation on sulphur in sulphates and sulphides. They showed that the isotope fractionation of sulphur in sulphates was constant at 1.020 when the supply of sulphate was limited in a closed system. Thus, regardless of the instantaneous concentration of sulphate, S^{32} will react 2% faster than will S^{34} . They also showed that the reaction is unidirectional and comparable to that expected from an inorganic reduction of sulphates. Harrison and Thode (1958) postulated that the bacterial reduction of sulphates caused fractionation of the sulphur in two possible ways, namely in the reduction of SO_4^{2-} to SO_3^{2-} there is first a combining step of the sulphate to an enzyme and then secondly the enzyme-sulphate bond is broken with the enzyme cleaving off an oxygen from the sulphate; i.e.,

STEP I



STEP II



They said that step I left behind S^{32} in the free sulphate ions and preferentially took up S^{34} . Then in step II, the oxygen cleavage step, the sulphate complex with S^{32} was

preferentially broken to SO_3^{2-} . This postulate is in accord with the general principle stated originally. Harrison and Thode showed at very low sulphate concentrations (1×10^{-5} moles/l) that step I became unidirectional in the c_1 direction and dominant, while at higher concentrations step II was dominant.

Biological reduction of sulphates have, in general, been shown to fractionate sulphur (when there is a fractionation) such that the residual sulphate is enriched in S^{34} (Yeremenko and Mekhtiyeva, 1961; Kaplan and Rittenberg, 1964; Jones and Starkey, 1957; Kaplan, Emery and Rittenberg, 1963; Nakai and Jensen, 1964; Mekhtieva and Kondrat'eva, 1966; Thode, Kleerekoper and McElcheran, 1951) except at very low sulphate concentrations. When, conversely, sulphate is being biologically synthesized it will be lighter in S^{34} than the source of sulphur (Nakai and Jensen, 1964).

2. Sulphate Distribution in Sediments

A simplified model of the distribution of sulphates in recent sediments was proposed by Berner (1964). Berner's model assumed that the local time rate of change of concentration of sulphate in the interstitial water of sediments was the sum of three terms:

- a. Ionic diffusion
- b. Deposition plus compaction
- c. Bacterial (anaerobic) sulphate reduction.

His solution was

$$C = (C_0 - C_\infty) e^{-\frac{(kx)}{w}} + C_\infty$$

where,

c = concentration of sulphates,

w = rate of deposition less rate of compaction and
is equal to dx/dt ,

k = carbon oxidation rate constant for sulphate
reducing bacteria,

x = depth (in the core in cms),

C_0 = initial concentration (at $x = 0$),

C_∞ = asymptotic concentration (at $x = \infty$).

Berner fitted his solution to sulphate concentrations in one of the cores of Kaplan et al (1963). This is reproduced as Figure 14. The equation for the fitted curve is

$$C = 19 e^{(-.015x)} + 8$$

Berner fudged a bit here since values of sulphate concentration increase after depths greater than 320 cm. Kaplan et al (1963) suggested that the asymptotic value for sulphate concentration at depth could be an artifact of analytical technique or could be a measure of the exhaustion of utilizable organic carbon. Nakai and Jensen (1964) showed that biological oxidation of sulphur and pyrite took at least 10 days. Thus Kaplan et al were probably wrong to suspect manipulation as a source of error. Two of the three cores analyzed by Kaplan et al showed a virtual monotonic decrease in sulphate concentration with depth. One (Santa Catalina - 6248) showed a zone of increasing sulphate concentration with depth in the first meter of the core, then a steady decrease

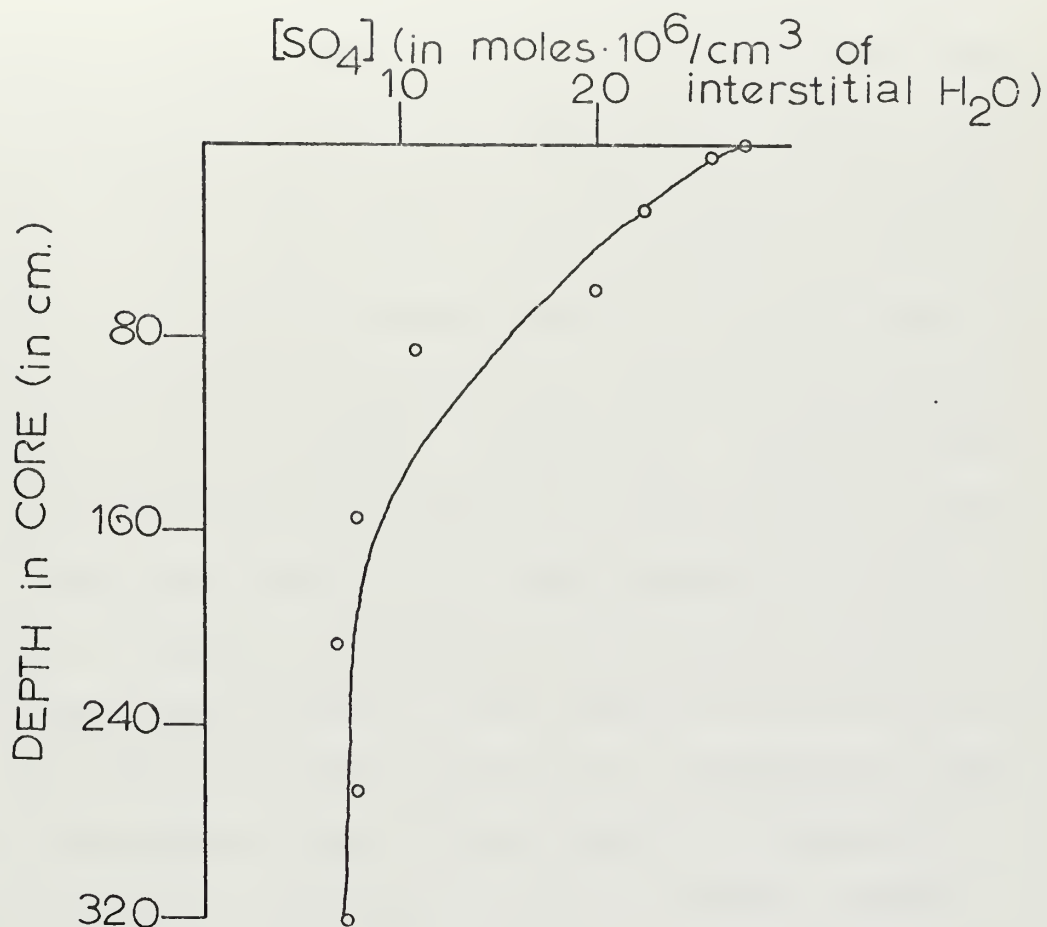


Figure 14. Sulphate concentration versus depth data for core 7131 from Santa Barbara Basin (after Kaplan et al, 1963).

in concentration until values were comparable to the other cores (Figure 15). The Kaplan group felt that the surface of the sediments is an area where aerobic bacteria are actively fractionating sulphur compounds, giving the sediment column a population of combined sulphur whose isotopic composition is significantly different from that of sea water sulphur whose $\delta S^{34} = 20.4 \text{ ‰}$. This concept is strongly supported by the work of Skerman (1969) who demonstrated co-populations of aerobes, anaerobes and sulphate-reducers in cores taken in Milford Sound, New Zealand. He found these three types of bacteria co-existing in ratios of 6:7:5 and 6:6:5 in the upper inch or two of the sediments. In one such core, co-existent populations of all three types of bacteria were demonstrated to exist down to 7 ft in an 8 ft core. The depth of aerobic activity was attributed to the strictly terrestrial origin of the deposits. Kaplan and Rafter (1964) also showed that surface sediments support Thiobacilli who draw O_2 from overlying waters and H_2S from the lower sediments by diffusion.

The sulphates in the Santa Monica and Santa Barbara cores (Kaplan et al, 1963) became enriched in S^{32} with depth while the Santa Catalina core showed a progressive enrichment in S^{34} (Figure 16). However, this data was scanty and showed only a trend with no details.

3. Isotope Ratios of Sulphates in a Core

Kaplan et al (1963) suggested a hypothetical model of the sulphur cycle in recent California sediments. They

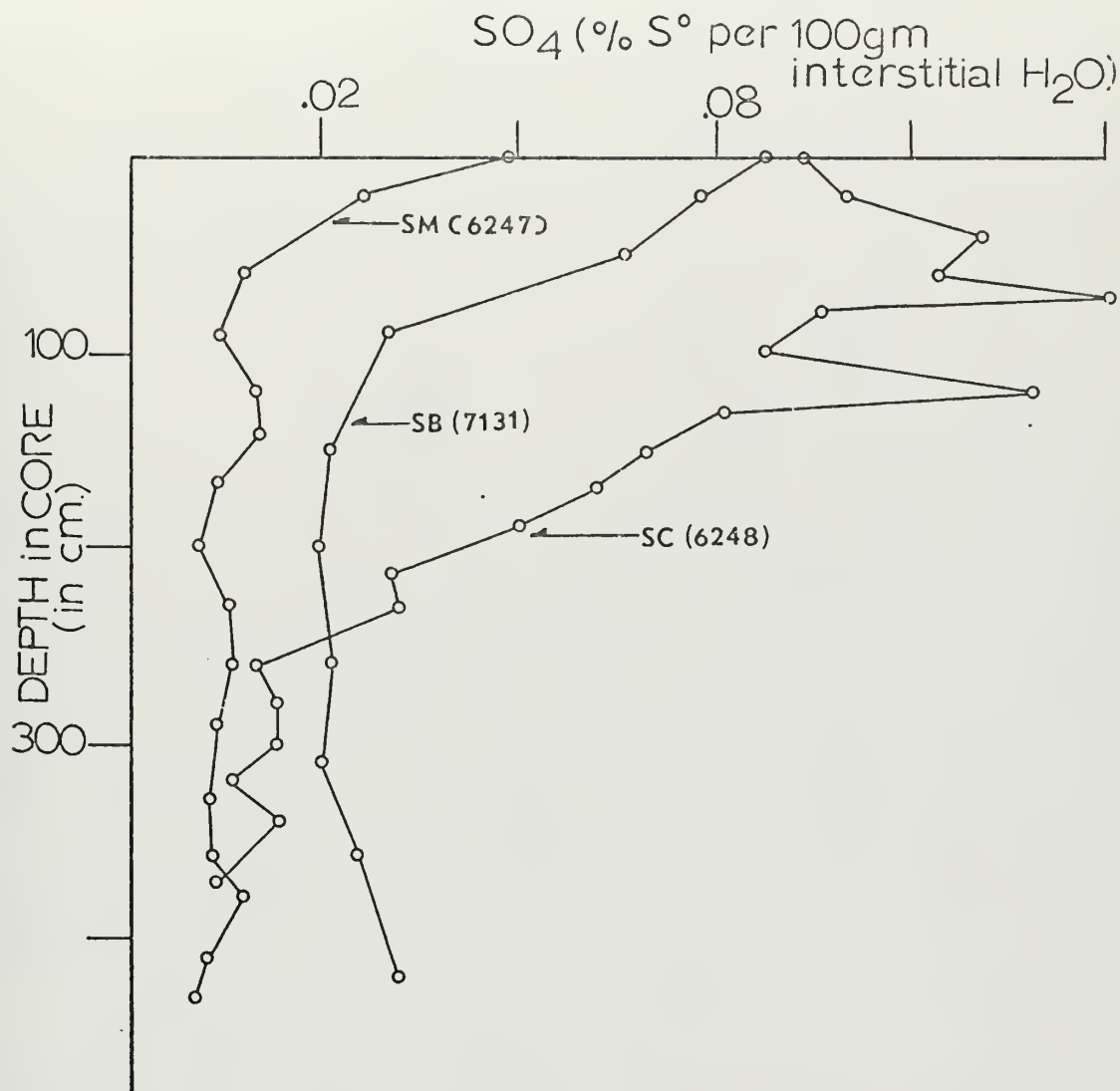


Figure 15. Sulphate concentration versus depth for three cores from California shelf (after Kaplan et al, 1963).

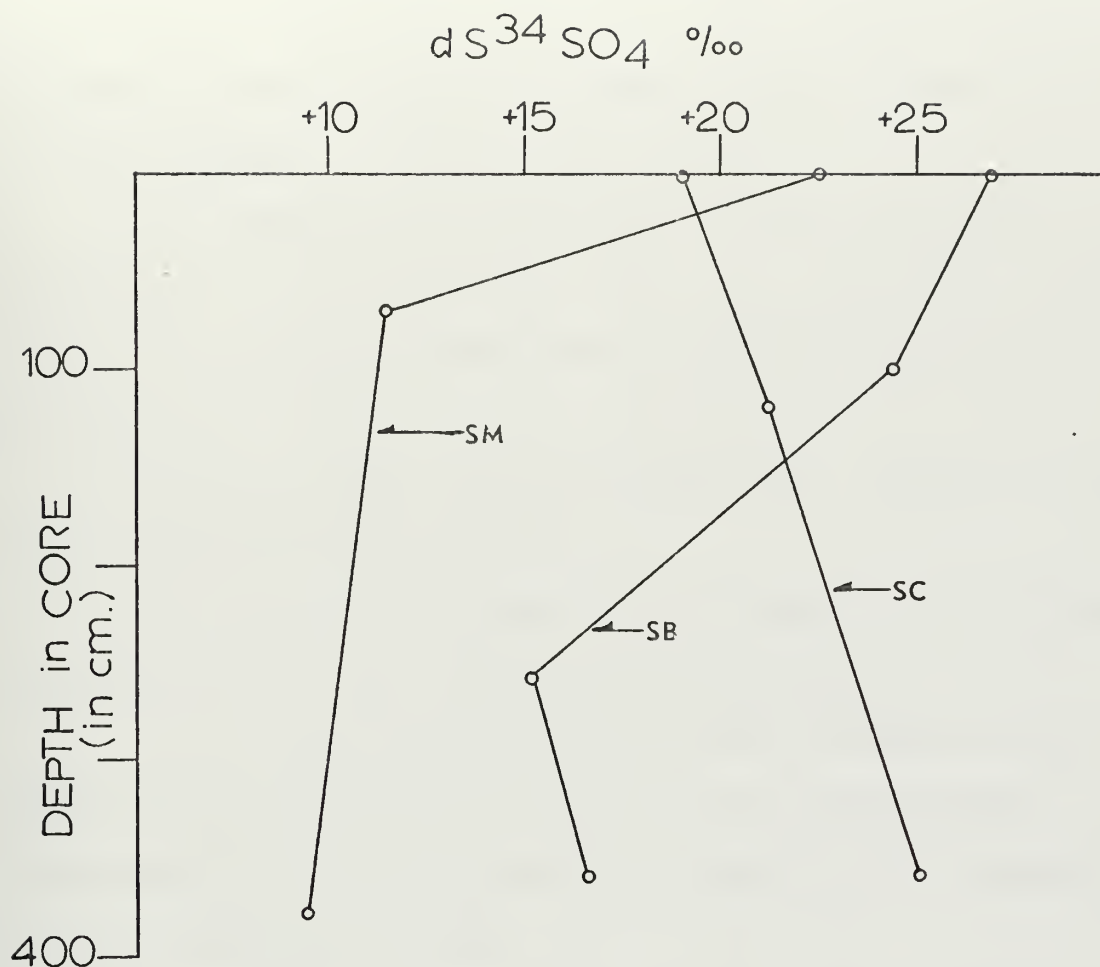


Figure 16. δS^{34} values for three cores from the California shelf (after Kaplan et al, 1963).

assumed:

- a. Constant rate of deposition.
 - b. Sulphate was present in the sediment column dissolved in the interstitial waters, not in combined form (barite, gypsum) or adsorbed onto clays.
 - c. There was no diffusion of water into the sediments from the overlying water; i.e., the water in the column is a closed system added to only by new deposits at the top.
 - d. At some time after deposition, oxygen was exhausted by microbial activity.
 - e. After the oxygen was all depleted, then sulphate reduction started and proceeded to completion.
 - f. A cascade of reactions then occurred to sulphides which ultimately gave pyrite as an end product.
- The consequences of this model, in terms of what happened to the sulphate were that:

The δS^{34} of sulphate sulphur would increase with depth and exceed that of sea water at all depths after the initiation of sulphate reduction.

To this model, certain modifications were added to explain their findings:

- a. At the sediment-water interface sulphate reduction (pyritization) could occur in microenvironments such as faunal tests. This pyrite, formed from the infinite sulphate pool of the overlying water, was depleted in S^{34} and could later serve as a source of light sulphur for the formation of light sulphate by sulphur-oxidizing reactions.

b. The isotopic enrichment in S^{34} was found to be inversely proportional to the rate of reduction. That is, the faster the rate of reduction, the less the fractionation between the parent sulphate and the product pyrite.

With regards to the oxygen ratios in sulphates, the following processes are therefore suggested as likely to occur:

a. At the sediment-water interface both aerobic and anaerobic bacteria can co-exist and can reduce and oxidize sulphur in relatively close proximity to each other. However, since the Thiobacilli have been shown not to fractionate elemental sulphur (Kaplan and Rittenberg, 1964; Jones and Starkey, 1957) in sulphate production and sulphides only weakly (Kaplan and Rittenberg, 1962; Kaplan and Rafter, 1958), it is assumed that their fractionation effect upon oxygen is also small or non-existent. This is perhaps a poor assumption but there is no other data bearing directly on the problem.

b. As sediment is buried more deeply in the core, its oxygen supply becomes more and more depleted by the action of Thiobacilli and the possibility for completely reducing microenvironments to occur would increase. Thus the sulphate is being more depleted in O^{16} and becoming heavier.

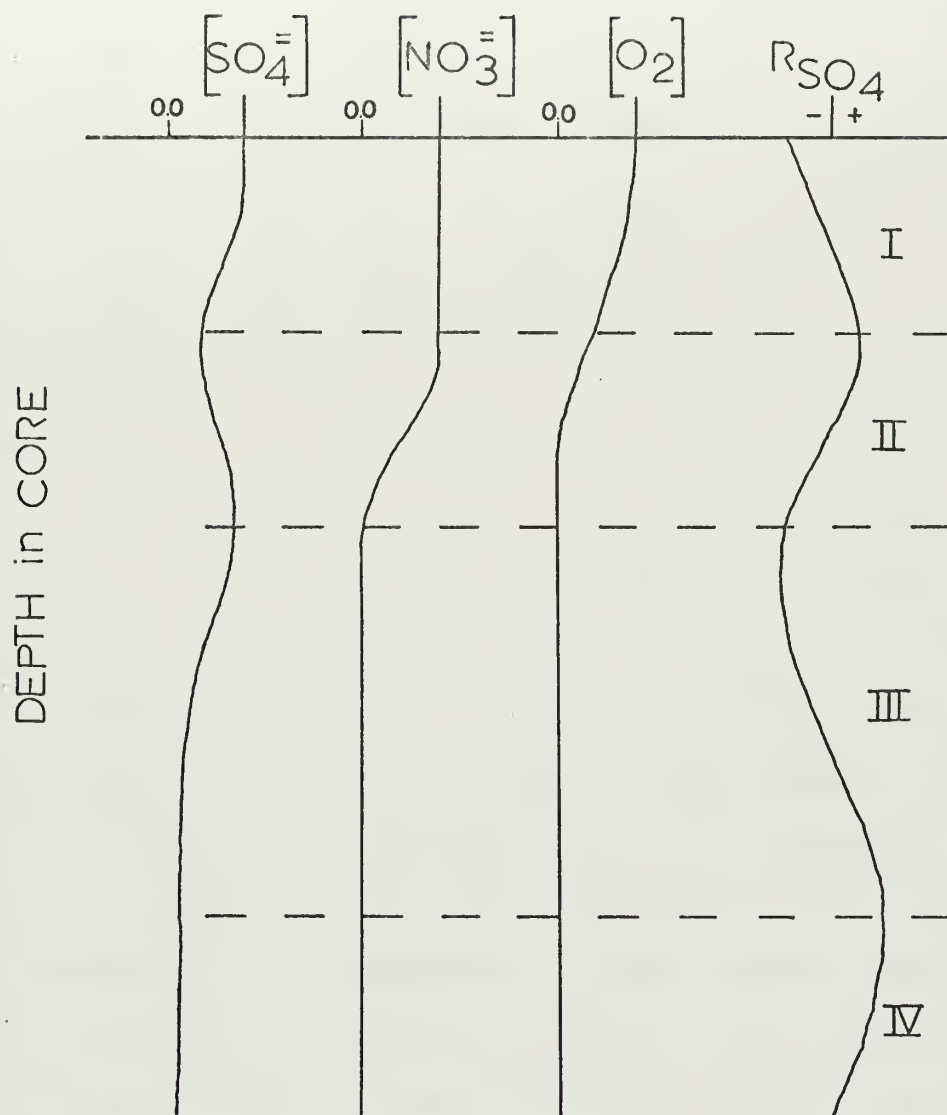
c. Nitrophilic bacteria could oxidize free sulphur to form sulphates using nitrates as an oxygen source. This reaction would probably only occur after all the oxygen was used up since free oxygen has a lower bonding energy than

nitrates, or may occur to an increasing extent in microenvironments. This sulphate so formed would be light in sulphur relative to the elemental sulphur which is itself light relative to the ambient sulphates. This is expected since each process from pyritization to sulphur oxidation results in a fractionation of the sulphur with the lighter S^{32} being preferentially acted upon. It is assumed that the sulphate so formed would similarly be lighter in oxygen than the nitrates from which it was formed. There does not appear to have been any work done on the oxygen exchange time constant for nitrates. Longinelli and Craig (1967) remarked that the nitrate time constant was presumed to be long but gave no further data. It is presumed that it is at least as long as that for sulphates.

d. The sulphate oxygen is, at each step, continuing the slow equilibration process with the water. After all other processes are subtracted out, a residual decline in the oxygen ratio approaching that of the ambient interstitial water should be noted.

e. The effect of organically bound sulphur on the sulphate system is ignored. Kaplan et al (1963) estimated that organically-bound sulphur constituted less than 1% of the total sulphur in the sediments.

The sum total of these processes, except time equilibration is presented as an idea-gram in Figure 17. This figure shows only a qualitative hypothetical model and does not take into account any other processes. From Figure



- | | |
|------------|--|
| Region I | Sulphate reducers ($\text{H}_2\text{O} + \text{CO}_2$); O_2 + sulphate producers ($-\text{H}_2\text{O}$) |
| Region II | Sulphate reducers ($\text{H}_2\text{O} + \text{CO}_2$); NO_3 + sulphate producers ($-\text{H}_2\text{O}$) |
| Region III | Sulphate reducers [step II of Harrison and Thode (1958) dominant] |
| Region IV | Sulphate reducers [step I of Harrison and Thode (1958) dominant] |

Figure 17. Idea-gram of nutrients and oxygen ratios versus depth. (Depth scale is arbitrary and concentrations of nutrients are arbitrary).

17 it can be seen that the sulphate concentration decreases with depth while being reduced and oxygen is being used up until nitrophilic bacteria start producing more, after which it monotonically decreases in concentration. It was noted qualitatively during sample handling that the amount of precipitate in the cores did decrease by a factor of about 5 from top to bottom of the cores.

4. Effect of pH on Oxygen Ratios

If no processes acted on the water or the sulphates, and the sulphates were initially heavier than the water by 9.5 ‰ (Longinelli and Craig, 1967), then one would expect the oxygen ratios to approach each other in a closed, constant volume system (Figure 18). The $\delta O^{18}H_2O$ and $\delta O^{18}SO_4$ should asymptotically approach each other and in time have a common del value between 9.5 and 0.0 per mille. Teis (1956) noted that the rate of equilibration is pH dependent. Increased CO_2 concentration speeds the equilibration. Lloyd (1967) noted this pH dependence and ran several of his samples at different pH's to determine its effect on the time rate of equilibration. From Longinelli's graph, one can determine that

$$\left. \frac{d(\log t_{1/2})}{d(pH)} \right|_{T^{\circ}C = \text{constant}} = 0.35$$

For instance, the half life Lloyd calculated for pH 7 was about 3 years (at 200°C) and was 50 years at pH 9 (at 200°C). Thus, if the pH in the sediment column is to change with depth (time), the rate of exchange will change correspondingly. In all levels of the previously discussed model,

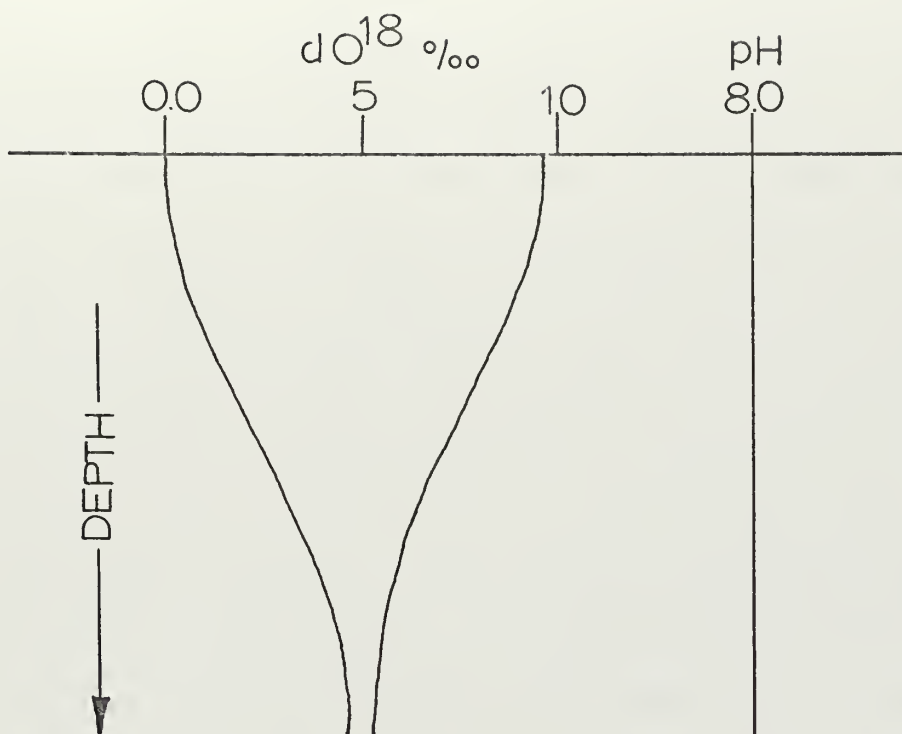


Figure 18. Idea-gram of δO^{18} versus depth (no pH variation).

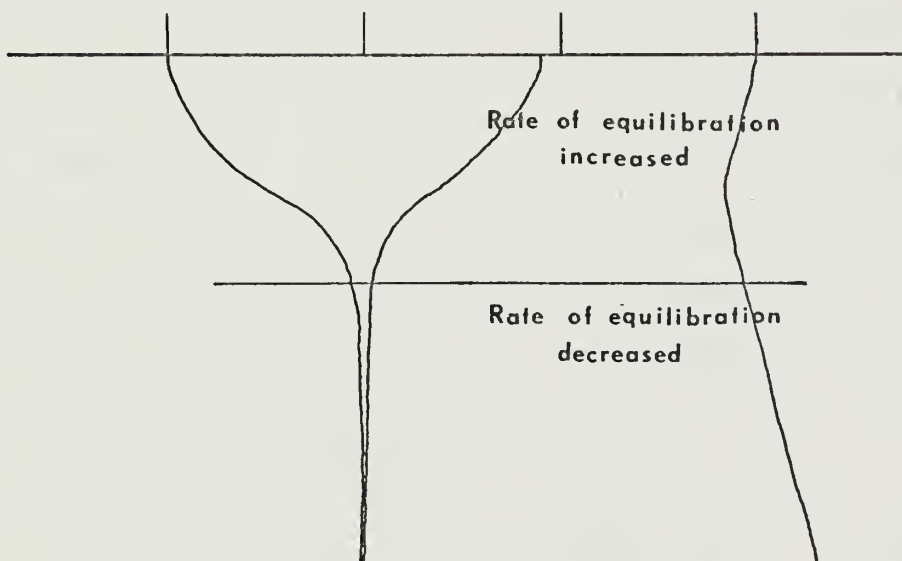


Figure 19. Idea-gram of δO^{18} versus depth (with pH variation similar to that found by Kaplan et al, 1963).

CO₂ is produced by bacterial action. This will quickly equilibrate with the interstitial water as well as change its pH. Kaplan et al (1963) noted an initial decrease in pH in the first 30-100 cm of core in their Santa Barbara, Santa Monica and Santa Catalina basin cores. Below that level the pH was erratic but generally increased slowly with depth to a value of about 8.0 (from 7.4). This can be interpreted to mean that the CO₂ being added to the core in situ below 100 cm by sulphate reducers was not sufficient to prevent the slow increase of the pH of the interstitial water in the core from other processes. The surface layers may have had so much sulphate that the CO₂ produced could significantly lower the pH as was reflected in their analysis. A generalized idea-gram of $\delta O^{18}SO_4$ versus depth is drawn in Figure 18. The effect of the expected variation of pH in a core upon the rate of oxygen isotope equilibration is to speed it up in the surface layers and to slow it down at depth. If it varies by 0.5 pH units, the time constant could be approximately halved. The effect of pH upon the del curves is idealized in Figure 19. In reality the effect of pH on the shape of the two isotope ratio curves may be very small over 30-100 cm of core.

In the surface layers and down to the bottom of the modeled nitrophilic zone, water is being used up by both nitrophiles and aerobic sulphate producers. Again one expects the lighter water to enter the reaction first. And we note that sulphate reducing bacteria respire water as a by product. Thus, exclusive of the time effect, the $\delta O^{18}H_2O$

will be a combination of these two biological reactions (Figure 20). Figure 20 assumes that sulphate reduction (water production) is proportional to the sulphate concentration and that sulphate production (water loss) is inversely proportional to the sum of the oxygen concentration and the nitrate concentration: i.e.,

$$d[H_2O]_a = K_1 [SO_4^{2-}]$$

$$d[H_2O]_b = K_2 [O_2 + NO_3^{2-}]$$

Thus,

$$d[\Sigma H_2O] = K_1 [SO_4^{2-}] + K_2 [O_2 + NO_3^{2-}]$$

The sulphate present in the top layers of both cores was noted as being lighter or at least the same as the sulphates in the overlying waters (Figure 6) and thus, water produced from their reduction would be lighter than the ambient interstitial water giving rise to an initial decrease in isotope ratio in the interstitial waters with depth. As the lighter sulphates were used up, the water became heavier and heavier. Down to 30 inches of core depth, data from core B-1 followed this hypothesis, below this (40 - 50 inches) it became dramatically lighter as though some new mechanism were then dominant. The ratios for sulphate (Figure 8) also shifted down and there was a decided loss of O^{18} from the water-sulphate system.

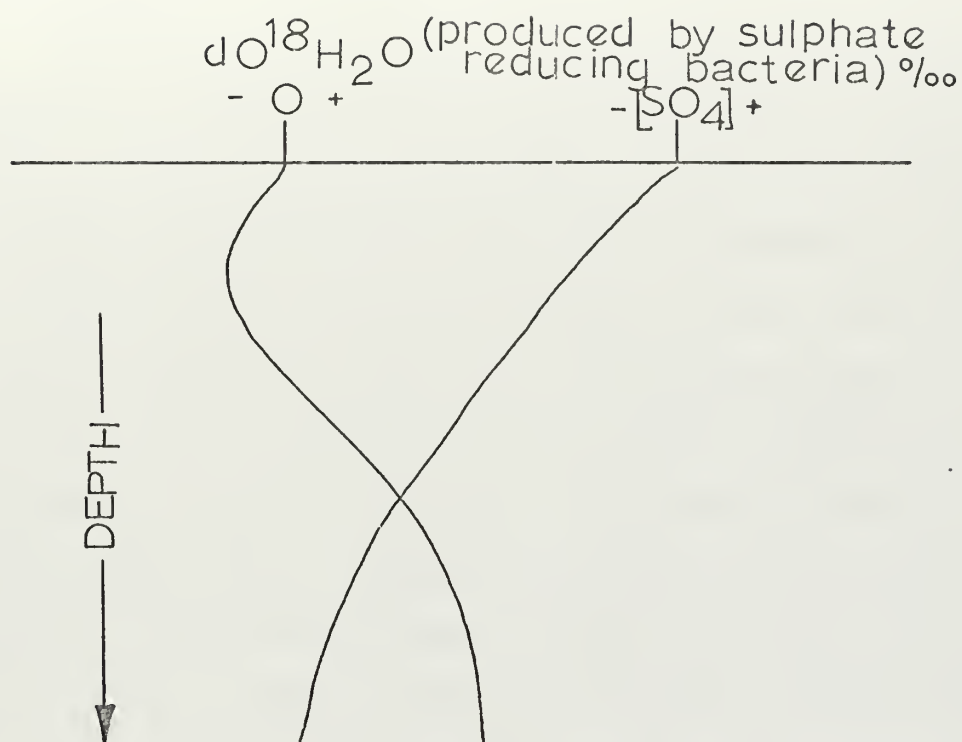


Figure 20. Idea-gram of $O^{18}(H_2O)$ and sulphate concentration versus depth as affected by sulphate-reducing bacteria.

5. Physical Processes Which Act on the Water-Sulphate System

Other processes acting on the water-sulphate system independent of anything thus far discussed cannot be exactly specified. Garlick and Dymond (1970) showed that volcanic glass shards do exchange O^{18} with water in sediments. They showed that probably the glass exchanges oxygen very slowly, altering the del value + 12 ‰ in 49 million years. Savin and Epstein (1970b) showed that there was no evidence of oxygen isotope exchange in detrital clay minerals from 24 worldwide ocean cores. However, authigenic montmorillonite was shown to fractionate oxygen relative to water in the ratio of 1.028 to 1.000. They stated, "when the minerals of an ocean sediment are formed in situ, this may be detected by their isotopic composition" (being different from the same mineral of detrital origin). They showed that minerals formed in a marine environment, "suggest formation in the marine environment under isotopic equilibrium conditions." In point of fact mixtures of minerals can be both lighter or heavier isotopically than their detrital counterparts. Siever (1968) showed that different clays reconstituted in silicate-spiked water could become less hydrous. Boron also has been shown to fractionate on adsorption to clays as boric acid (Schwarz, Aguei and McMullen, 1969).

Kaplan, Sweeney and Nissenbaum (1969) analyzed several cores from the Red Sea hot brine deeps for sulphur compounds and sulphur ratios. Figure 21 is a histogram of

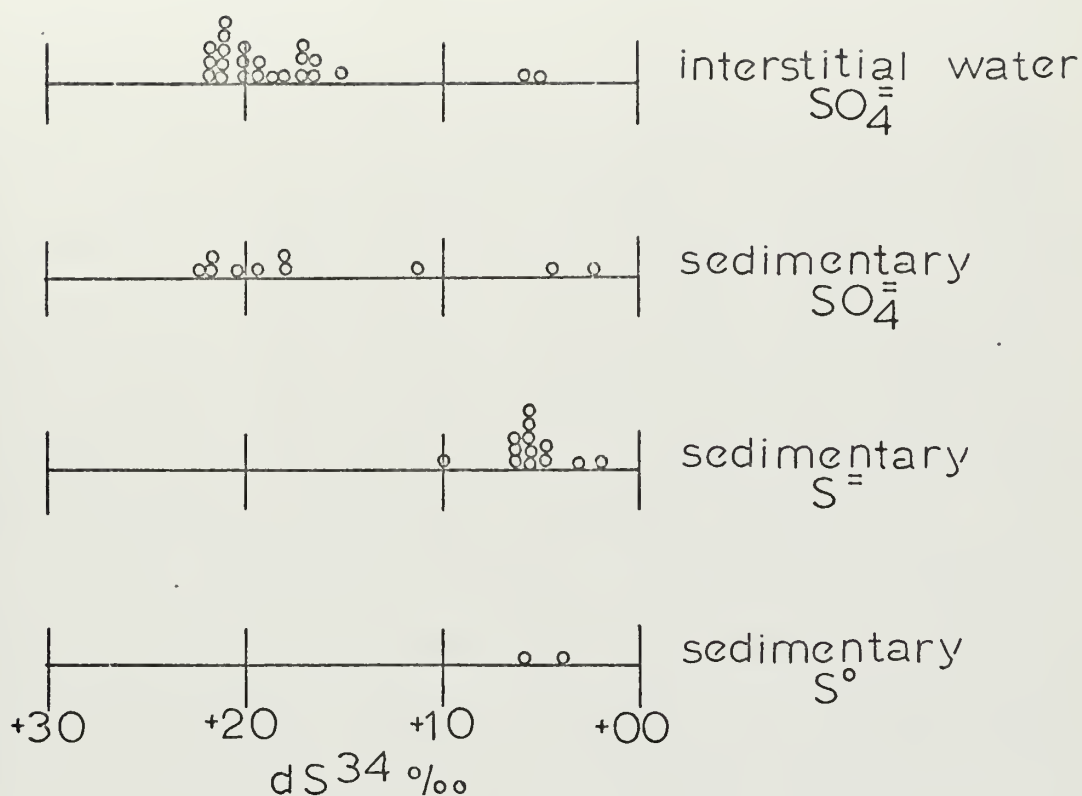
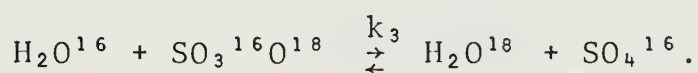


Figure 21. Histogram of sulphur isotope distribution of different sulphur species from interstitial water and sediment from Atlantis II Deep in the Red Sea (cores 84k and 120k) (after Kaplan, Sweeney and Nissenbaum, 1969).

their data from those cores taken from the Atlantis II Deep whose sediments have been shown to be sterile (Watson and Waterbury, 1969; Trüper, 1969). The interstitial sulphate was being fractionated when it entered the solid phase and, further, the sedimentary and interstitial sulphates were being fractionated by the physical processes which change them to sulphides and elemental sulphur. These processes were apparently step processes as a range of values for S^{34} were not found in the cores. In any event some magnitude of the changes to the sulphur population can be obtained from this. It is expected that the oxygen population would show corresponding responses to physical processes.

The effects of all of the processes discussed is diagrammatically depicted by Figure 22. There are three processes which are capable of adding O^{16} to sulphates in the interstitial water of a core section; they are:

- a. Biological oxidation of H_2S to sulphate by aerobic bacteria
- b. Biological oxidation of H_2S to sulphate by nitrophilic bacteria
- c. Time dependent equilibration with water



There are two processes which can remove O^{16} from the sulphates of a core sample; they are:

- a. Biological reduction of sulphates
- b. Chemical oxidation of H_2S (aerobically).

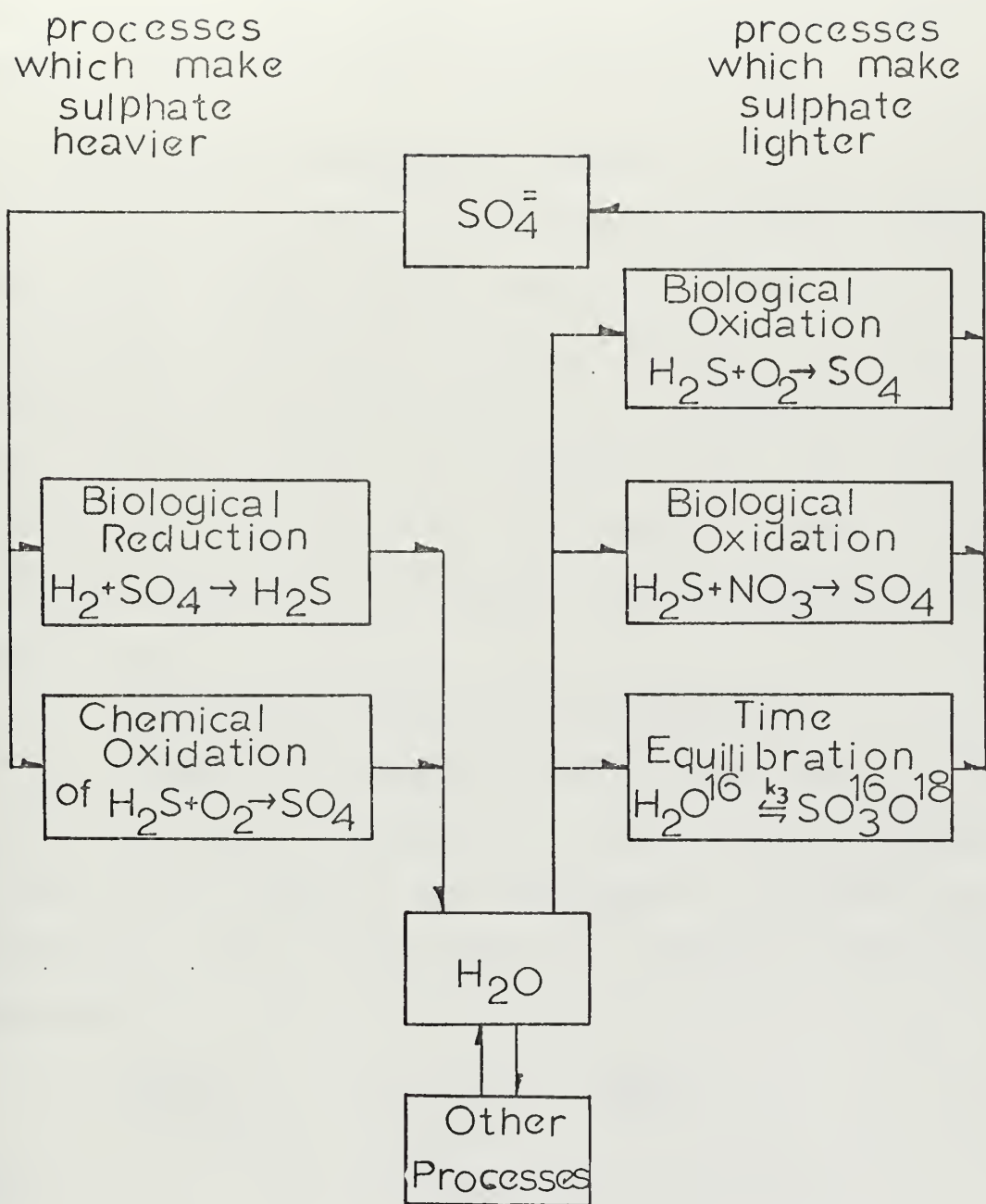


Figure 22. The water-sulphate oxygen isotope system in sediments. (Arrows indicate preferential movement of O^{16} .)

These same five reactions operate on water in an inverse fashion to alter the oxygen isotope ratio R_{H_2O} . In addition, other processes can operate to add or subtract O^{16} from the water. Examples of these were discussed above.

B. DEVELOPMENT OF MATHEMATICAL MODEL

The possible effect of nitrophilic bacteria, diffusion, reduction of organic sulphur compounds and very low sulphate concentrations will not be considered further. It was assumed that in core B-1 the zone 10 to 50 inches was anaerobic; thus, aerobic reactions were excluded. This left biological reduction of sulphates, time equilibration of water-sulphates and other processes to be considered in developing a mathematical model.

1. Effect of Sulphate-Reducing Bacteria

Kaplan and Rittenberg (1964) showed that the amount of fractionation of sulphate S^{34} is inversely proportional to the rate of reduction and independent of sulphate concentration. Such a relationship was presumed to hold for oxygen ratios:

$$\left. \frac{\partial R_{SO_4}}{\partial t} \right|_{\text{biol}} = k_1 \frac{1}{R_{SO_4}} = - \left. \frac{\partial R_{H_2O}}{\partial t} \right|_{\text{biol}} \quad (1)$$

where k_1 = proportionality constant.

2. Effect of Other Processes

The rate of change of the oxygen ratio in water due to other processes was arbitrarily assumed to be proportional to the rate of clay formation and had a fractionation factor

of 1.028 (after Savin and Epstein, 1970a):

$$\left. \frac{\partial R_{H_2O}}{\partial t} \right|_{o.p.} = \pm k_2 \frac{\partial c}{\partial x} w \quad (2)$$

where

c = concentration of authigenic materials

$w = dx/dt$ = rate of compaction rate of deposition

$k_2 = 1.028$.

3. Effect of Time Equilibration

The rate of equilibration of sulphate with water was taken to be proportional to the difference of the oxygen ratios of water and sulphate:

$$\left. \frac{\partial R_{SO_4}}{\partial t} \right|_{time} = -k_3 (R_{SO_4} - R_{H_2O}) = \left. \frac{\partial R_{H_2O}}{\partial t} \right|_{time} \quad (3)$$

where k_3 = time constant.

4. Computational Model

Now some expression was needed to express the concentration of authigenic minerals with depth. It was assumed that the change of concentration with time was proportional to the concentration of free interstitial water present, as suggested by the necessity of the presence of water for authigenic mineral formation (Siever, 1968; Savin and Epstein, 1970a). Further, the rate of compaction plus the rate of deposition was assumed constant with depth:

$$\frac{dx}{dt} = \text{constant}$$

$$\therefore \frac{\partial c}{\partial t} \frac{dx}{dt} = \frac{\partial c}{\partial t}$$

and

$$\frac{\partial c}{\partial t} = k_4 [H_2O] \quad (4)$$

where k_4 = proportionality constant.

Figure 23 represents the moisture content of a core taken by Kaplan et al (1963). It can be seen that the moisture content decreases with depth. The Santa Barbara core (7131) had a nearly constant composition of clay/silt with depth and thus probably represented as uniform a core as one could obtain. The clay/silt content of core A-2 (Figure 24) was nearly the same as that of the Santa Barbara core.

An exponential curve was fitted to the Kaplan data presuming that the water content was being progressively used up. The equation for this curve is:

$$[H_2O] = e^{-0.00774x} \text{ gm/gm}$$

where

$$x = \text{depth in cm}$$

$$K_w = 0.774 \times 10^{-2}.$$

Referring to equation (4) one can write

$$\frac{\partial c}{\partial t} = k_4 e^{-K_w \cdot x}$$

and substitution into equation (2) gave

$$\left. \frac{\partial R_{H_2O}}{\partial t} \right|_{o.p.} = k_2 k_4 e^{-K_w \cdot x} \quad (5)$$

Combining (1) and (3) to give the total time rate of change of the sulphate ratio gave

$$\frac{dR_{SO_4}}{dt} = k_1 \frac{1}{R_{SO_4}} - k_3 (R_{SO_4} - R_{H_2O}) \quad (6)$$

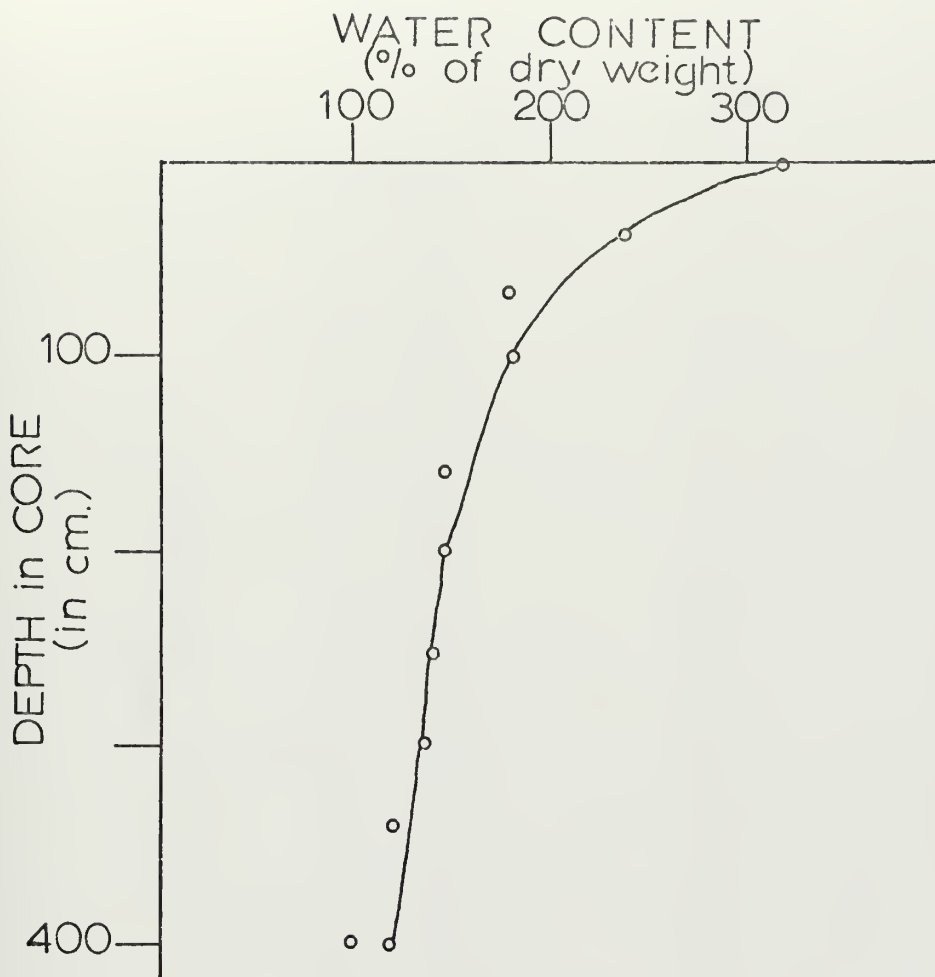


Figure 23. Moisture content of a core (after Kaplan et al, 1963).

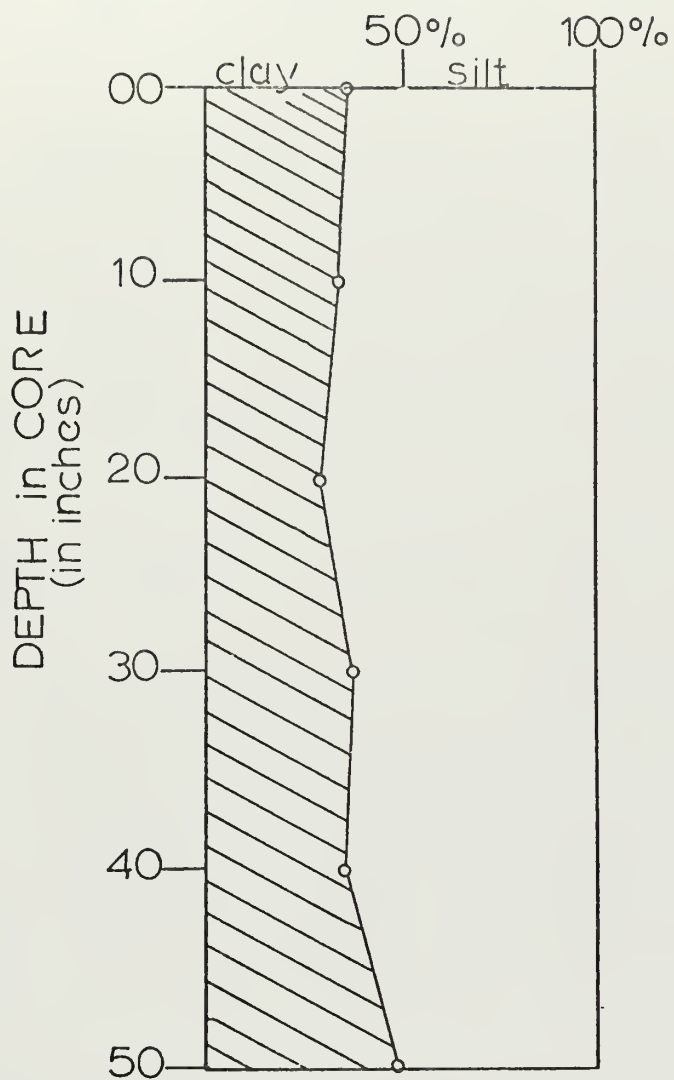


Figure 24. Clay versus silt for core A-2.

Similarly, for water ratios, combining equations (1), (3) and (5) gave

$$\frac{dR_{H_2O}}{dt} = -k_1 \frac{1}{R_{SO_4}} + k_2 k_4 e^{-K_w \cdot x} - k_3 (R_{SO_4} - R_{H_2O}) \quad (7)$$

Equations (6) and (7) are expressions representing the effects upon the water-sulphate system by bacteria, physical processes (authigenic mineral formation), and time rate of equilibration. These equations, when added together, give a computational equation to derive the time constant sought, k_3 ;

$$\frac{dR_{SO_4}}{dt} + \frac{dR_{H_2O}}{dt} = k_2 k_4 e^{-K_w \cdot x} - 2k_3 (R_{SO_4} - R_{H_2O}) \quad (8)$$

The analysis of core A-2b showed that there was little likelihood that a significant portion of the O^{18} in the water-sulphate system was being lost to the formation of authigenic minerals or other physical processes. Therefore, the first term on the right side of equation (8) was dropped leaving:

$$\frac{dR_{SO_4}}{dt} + \frac{dR_{H_2O}}{dt} = -2k_3 (R_{SO_4} - R_{H_2O}) \quad (9)$$

in which k_3 is the looked for time constant for sulphates in years $^{-1}$.

Berner (1964) assumed that the deposition rate for recent California shelf sediments was about 0.30 cm per year. If this rate is assumed to be approximately true, then each 10 inches of core segment represented 84.5 years. This was

adopted as the time scale for core B-1. A pelecypod shell was found at the bottom (50 inches) of core B-1 and, if it were possible to have it analyzed for age by C^{14} analysis, the time scale assumed above could be revised accordingly. However, such an analysis was not available. Core B-1 then was assumed to represent a time series 422.5 years old. This was incorporated in Figure 25.

With each time step being 84.5 years, the computational model became

$$\frac{\left[-R_{SO_4} \Big|_{t_1} + R_{SO_4} \Big|_{t_2} - R_{H_2O} \Big|_{t_1} + R_{H_2O} \Big|_{t_2} \right]}{84.5 \left[R_{SO_4} \Big|_{t_1} - R_{SO_4} \Big|_{t_2} - R_{H_2O} \Big|_{t_1} + R_{H_2O} \Big|_{t_2} \right]} = k_3 \text{ years}^{-1} \quad (10)$$

Equation (10) utilized simple difference molecules for the time rate of change of the sulphate and water ratios and arithmetic averages for the absolute ratio differences. The computed k_3 's are presented in Table 9. The first 10 inches of the core was apparently undergoing processes which were, as expected, contrary to the assumptions made in the mathematical model and thus was disregarded. The average of the rest of the data gave a value of

$$k_3 = -0.0150 \pm 0.0029 (\text{standard deviation}) \text{ years}^{-1}$$

The value of k_3 is negative since the ratios decrease each year.

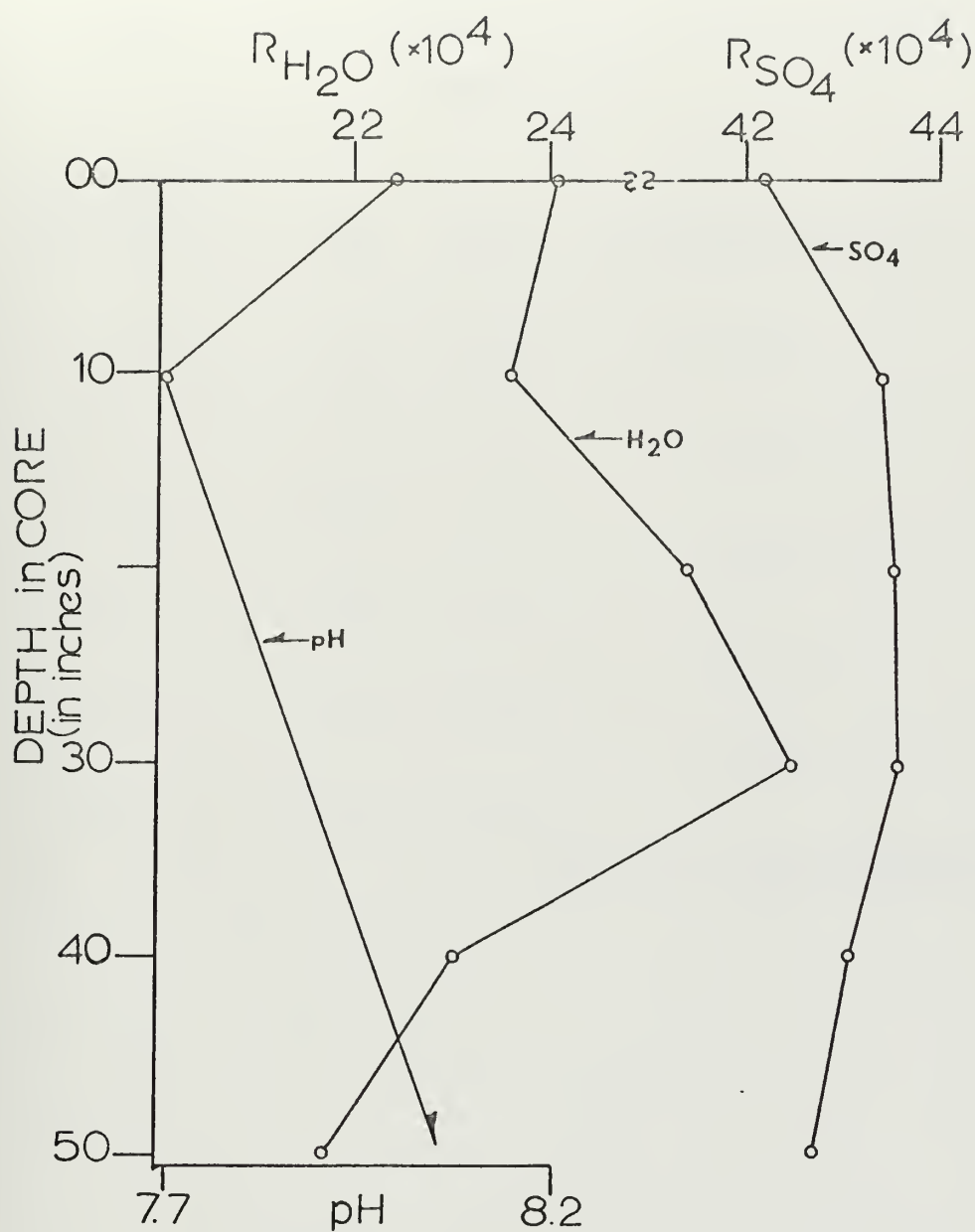


Figure 25. Combined parameters of core B-1.

Table 9
Values of Time Constant Derived From Evaluation of
Equation (9)

Core Depths (Inches) (Core B-1)	R_{SO_4}	R_{H_2O}	Time Constant (k_3)
0 - 2	42.2	24.1	-0.00465
10	43.4	23.6	0.0134
20	43.5	25.4	0.0118
30	43.5	26.5	0.0151
40	43.0	23.0	0.0195
50	42.7	21.7	
Average $0.0150 \pm 0.0029 \text{ years}^{-1}$			

5. Calculation of $t_{\frac{1}{2}}$

Referring back to equation (3), the value of the half life ($t_{\frac{1}{2}}$) of the sulphate oxygen was finally computed,

$$\left. \frac{dR_{SO}}{dt} \right|_{\text{time}} = k_3 (R_{SO_4} - R_{H_2O}) \quad (3)$$

The solution to this ordinary differential equation is

$$\ln (R_{SO_4} - R_{H_2O}) = k_3 \Delta t \quad (11)$$

When the argument of the log term on the left is $\frac{1}{2}$, then $t=t_{\frac{1}{2}}$ and,

$$t_{\frac{1}{2}} = 46.2 \text{ years}$$

This is approximately two-thirds the value which Teis (1956) obtained of 70 years and three orders of magnitude less than what Lloyd (1967) obtained. The figure of 46.2 years is inversely proportional to the estimate of the time scale assumed. Therefore, it appeared that Teis' estimate was closer to what may be found in the real ocean.

The Lake Vanda study (Rafter and Mizutani, 1967) showed that the sulphates were changing their oxygen isotope ratios more rapidly than was the water. This may indicate that the physical processes acting on the water were operating in the opposite direction then the other biological processes.

Further work remains to define more accurately the oxygen cycle in sulphates in sediments and the ocean so that more accurate relationships than equations (6) and (7) can be formulated.

V. SUMMARY

The original intent of this paper was to determine the time constant for the rate of equilibration of oxygen in sulphates with water. This was done experimentally using two cores from the upper Carmel Canyon as a time series. The interstitial sulphates and the interstitial waters were analyzed for their oxygen isotope ratios on a mass spectrometer. Next, the various biological and physical processes which can act on sediments to alter the water-sulphate system isotopically were reviewed and discussed. These processes were:

a. Biological reduction of sulphate by sulphate-reducing bacteria (Desulfovibrio sp.).

b. Biological oxidation of sulphur compounds by aerobic sulphate-reducing bacteria (Thiobacilli sp.).

c. Biological oxidation of sulphur compounds by an aerobic sulphate producing bacteria (e.g., Thiobacilli denitrificans).

d. Chemical oxidation of sulphur compounds aerobically.

e. Other physical processes which act to alter oxygen isotope ratios of water which do not affect the sulphate oxygen ratios (e.g., authigenic mineral formation).

f. The time rate of equilibration of the oxygen ratios of the water-sulphate system.

A mathematical model was proposed which had terms modeling those processes considered significant in the anaerobic zone of a sediment column. These processes were a, e and g above. The two differential equations thus obtained were manipulated to yield a computational model which gave the time constant for the oxygen ratios of sulphate of,

$$-0.0150 \pm 0.0029 (\text{standard deviation}) \text{ years}^{-1}$$

This was then used to determine the half life of sulphate oxygen ratios as

$$t_{\frac{1}{2}} = 46.2 \text{ years}$$

which was in fair agreement with Teis' (1956) work but three orders of magnitude different from Lloyd's (1967) work. Once such constants can be precisely determined as a function not only of time but of pH and biological processes as well, investigators will have another powerful dating tool available for water mass age determinations which will not require the use of radioactive nuclide techniques.

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13. ABSTRACT			

An investigation was made into the rate of equilibration of the stable isotopes of oxygen in the water-sulphate system in the ocean. Two cores from the Carmel Submarine Canyon off the California coast were analyzed. The absolute ratios of the oxygen in the interstitial water and dissolved sulphates were determined using a mass spectrometer. The various biological and physical processes which can alter the isotopic ratios were discussed and a simple mathematical model was proposed. The mathematical model retained terms which were considered significant in the anaerobic zone of a sediment. After simple manipulations, a computational model was derived and a time constant for the oxygen ratio of the water-sulphate system was determined as -0.0150 ± 0.0029 (standard deviations) year⁻¹. From this, the $t_{1/2}$ was determined to be 46.2 years.

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KEY WORDS

LINK A

LINK B

LINK C

ROLE

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Sulphate Oxygen Ratios

Oxygen Ratios

Water-Sulphate System in Sediments

Stable Oxygen Isotope Ratios

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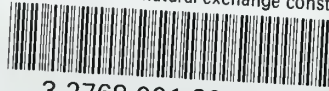
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